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1	WHC-SD-EN-TI-112	N/A	0	Vadose Zone Modeling of Carbon Tetrachloride in 200 West Area at the Hanford Site	4	1/2	1	

16. KEY

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1	1	Cog. Mgr. A. J. Knepp 3/9/93 H6-06	ERC L6-07	3	
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WHC-SD-EN-TI-112, Rev. 0

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Title Vadose Zone Modeling of Carbon Tetrachloride in 200 West Area at the Hanford Site

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SUPPORTING DOCUMENT

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6. Author

Name: A.G. Law

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7. Abstract

This report describes the vadose zone flow simulations conducted in FY1992 for evaluating the migration of carbon tetrachloride from the 216-Z-9 Trench. The results suggest that carbon tetrachloride could have migrated to the water table from the trench, but the results will remain tenuous until several uncertainties are investigated further. Recommendations are made for resolving these uncertainties in work underway in FY1993.

Piepho, M. G., A. G. Law, M. P. Connelly, K. A. Lindsey, 1993, *"Vadose Zone Modeling of Carbon Tetrachloride in 200 West Area of the Hanford Site"*, WHC-SD-EN-TI-112, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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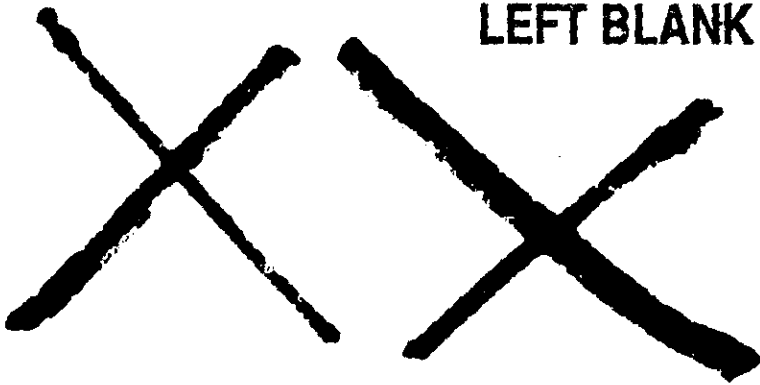
EXECUTIVE SUMMARY

Flow simulations performed to date suggest that it is possible that carbon tetrachloride (CCl_4) may have migrated to the water table from the 216-Z-9 Trench irrespective of whether an unsealed borehole may have provided a direct pathway for contaminants to reach ground water. However, this result should be viewed as tenuous as no data on non-aqueous phase liquid (NAPL) residual saturation is available at the present, and several simplifications applied in the simulations to date require further investigation. Graphs depicting the simulated movement of water and liquid CCl_4 are presented in the body of this report.

During FY 1992, difficulties in the application of the SAMFT2D code on the Cray (a trademark of Cray Research Inc.) computer were resolved, and it is now operational on the Hanford Site Cray computer. After investigating the effects of four relative permeability relations, the two Stones' methods have been discarded in favor of the van Genuchten and Brooks-Corey relations combined with the extended Mualem theory. Since van Genuchten parameters are more readily available for Hanford Site sediments, the van Genuchten relationships will be used in future modeling endeavors.

The three-phase flow simulations suggest most of the free liquid CCl_4 that has not evaporated should now be located in the Plio-Pleistocene (caliche) layer and Early Palouse layer or in the ground water. Horizontal spread in the vadose zone appears to be minimal even though anisotropy was assumed. Two uncertainties that could affect these results are the effect of the dip (inclination) of the Early Palouse and Plio-Pleistocene layers (the layers were treated as horizontal in this study) and the assumed initial moisture content within the geohydrologic units of the unsaturated zone. These simplifications will be pursued in FY 1993 to evaluate how they influence the movement of water and liquid CCl_4.

In addition to evaluating the effect of the simplifications introduced to date, work planned for FY 1993 is the simulation of the movement of water, liquid CCl_4, gaseous CCl_4, and air in the vadose zone at the 216-Z-9 Trench, 216-Z-1A Tile Field, and 216-Z-18 Crib. These simulations will be accomplished through a transport simulation with SAMFT2D treating the gaseous phase of CCl_4 as a component of the air phase.

Accomplishment of these recommendations in FY 1993 should permit a reasonable estimation of where the CCl_4 is located in the subsurface environment, including predictions of the phases and concentrations. In addition, references have been identified that appear to provide methodology for determining if CCl_4 exists as a NAPL at residual saturation in the vadose zone, and perhaps determining its magnitude. Accomplishment of this task is necessary to provide a calibration of the simulation and to provide a measure of confidence in the results.

CONTENTS

FIGURES:

FIGURES (Cont.):

FIGURES (Cont.):

TABLES:

1.0 INTRODUCTION

Carbon tetrachloride (CCl_4) was used in processing operations in Z Plant during the period 1955 to 1973. Large quantities of CCl_4, which were disposed of to the ground via crib disposal facilities during this period, are now the subject of an expedited response action (ERA) to remediate CCl_4 vapors in the vadose zone (Hagood and Rohay 1991).

Vadose zone modeling is being employed to estimate the extent and concentration of the CCl_4 contamination and to attempt to identify the phase in which it may be found (Hagood and Rohay 1991). This information is to provide guidance for the ERA action in designing a remediation system.

The current state-of-the-art in dealing with organics in the subsurface environment is in its infancy. Methods for the measurement of organics in the subsurface; modeling of multi-phase flow and transport, especially in the vadose zone; and techniques of remediation are subjects of research and development. Additional complications in the application to the Hanford Site are the long length of time since disposal of the CCl_4, the condition of the transport lines from the processing building to the disposal cribs, the lack of information on the quantities and frequencies of disposal, and the unknown chemistry of the effluent streams at the time of the disposal. Even with these limitations it is expected that the modeling process will be able to contribute to an understanding of where the CCl_4 may be, what phase it may be in, and what the concentrations might be.

Because of the limited state-of-the-art in modeling multi-phase flow and transport in the vadose zone, it was decided that the approach to be taken would be to start out with a simple situation and then add complicating conditions one step at a time. Therefore, one disposal facility was selected for modeling, and the initial step was to model flow in the vadose zone considering that the effluent was composed of only a single phase, water. On the successful completion of that step the effluent would then be treated as a two-phase fluid: water and liquid CCl_4; and finally the effluent would be treated as a multi-phase fluid: water, air, liquid CCl_4, and gaseous CCl_4.

While the primary interest in this report is on the vadose zone, it is desirable to account for the estimated quantities of CCl_4 disposed of to the ground, which leads to an interest in the ground water or saturated zone. While no modeling of ground water was performed, literature on the movement of DNAPLs under saturated flow conditions, as well as unsaturated conditions, was reviewed to better understand the processes taking place under both conditions.

Prior to discussing the vadose zone modeling results, this report will briefly review disposal operations at the Hanford Site and factors affecting the migration of immiscible fluids in the subsurface environment. It is important to understand the processes affecting the migration of organic constituents as the modeling process is merely a mathematical representation of the physical and chemical processes controlling the movement of these constituents. Chapter 5.0 contains bibliographical information on the literature cited in this report. As a source for future reference, Chapter 6.0 includes listing a number of pertinent documents that have been collected.

1.1 REVIEW OF PROCESSING OPERATIONS AND WASTE DISPOSAL SITES

As noted in the ERA project plan (Hagood and Rohay 1991), information on the source term is to be collected for use in the modeling activity. This section is a summary of this information.

The CCl_4 disposal sites are located in the 200 West Area where chemical processing plants have been operating since 1944. The primary CCl_4 disposal sites are the 216-Z-1A Tile Field, 216-Z-9 Trench, and 216-Z-18 Crib (Figure 1). These facilities received liquid waste from the Z Plant [now Plutonium Finishing Plant (PFP)] facility operations. The 216-Z-9 Trench operated from 1955 to 1962, receiving organic solvent and aqueous waste from the RECUPLEX facility. The 216-Z-1A Tile Field received aqueous and organic waste from the Plutonium Reclamation Facility (PRF) from 1964 to 1969, after receiving only overflow liquid waste (no organics) between 1949 and 1959. From 1969 to 1973 aqueous and organic waste from PRF was disposed to the 216-Z-18 Crib.

The organic waste was principally CCl_4 but also contained other organic compounds, primarily tributyl phosphate (TBP). Adjustments in the reported volumes have been made to account for the TBP, but information is not available for the other organic compounds. Therefore the modeling is being performed assuming that the organic component of the total discharge is pure CCl_4. The organic component was much smaller than the aqueous volume, as may be observed in Figure 2 for discharges to the 216-Z-9 Trench.

It is estimated that a total of 363,000 to 580,000 L of CCl_4 was discharged to the soil column between 1955 and 1973 at the three sites mentioned previously. As a breakdown for each of the three sites, it is estimated that the 216-Z-9 Trench received 83,000 to 300,000 L, the 216-Z-1A Tile Field received 170,000 L, and the 216-Z-18 Crib received 110,000 L. More detailed information on these discharges may be found in Appendix B of DOE-RL (1991).

The 216-Z-9 Trench was selected as the disposal facility for initial modeling of the CCl_4 in the vadose zone. This facility had the smallest area of the three facilities and received the largest quantity of CCl_4 per unit of area. Also it did not have any complicating conditions, such as the 216-Z-1A Tile Field which received waste water effluent for 10 years prior to receiving the organic waste.

1.2 REVIEW OF MIGRATION OF IMMISCIBLE FLUIDS IN THE SUBSURFACE ENVIRONMENT

Carbon tetrachloride is one of a number of organic compounds that does not mix easily with water (i.e., it is "immiscible"), and therefore may be found as a "free or pure phase" in the environment. This is commonly referred to as a "non-aqueous phase liquid" or NAPL. Carbon tetrachloride is more dense than water and therefore it belongs to a class of compounds known as DNAPLs, or "dense non-aqueous phase liquids." (Note: The term "heavy immiscible liquid" or HIL is sometimes used also.) Carbon tetrachloride is also quite volatile and therefore readily observed in the gaseous state. The task of tracking the migration of CCl_4 is therefore one of dealing with the

Figure 1. 200 West Area Showing Location of Liquid Waste
Disposal Facilities That Received Carbon Tetrachloride.
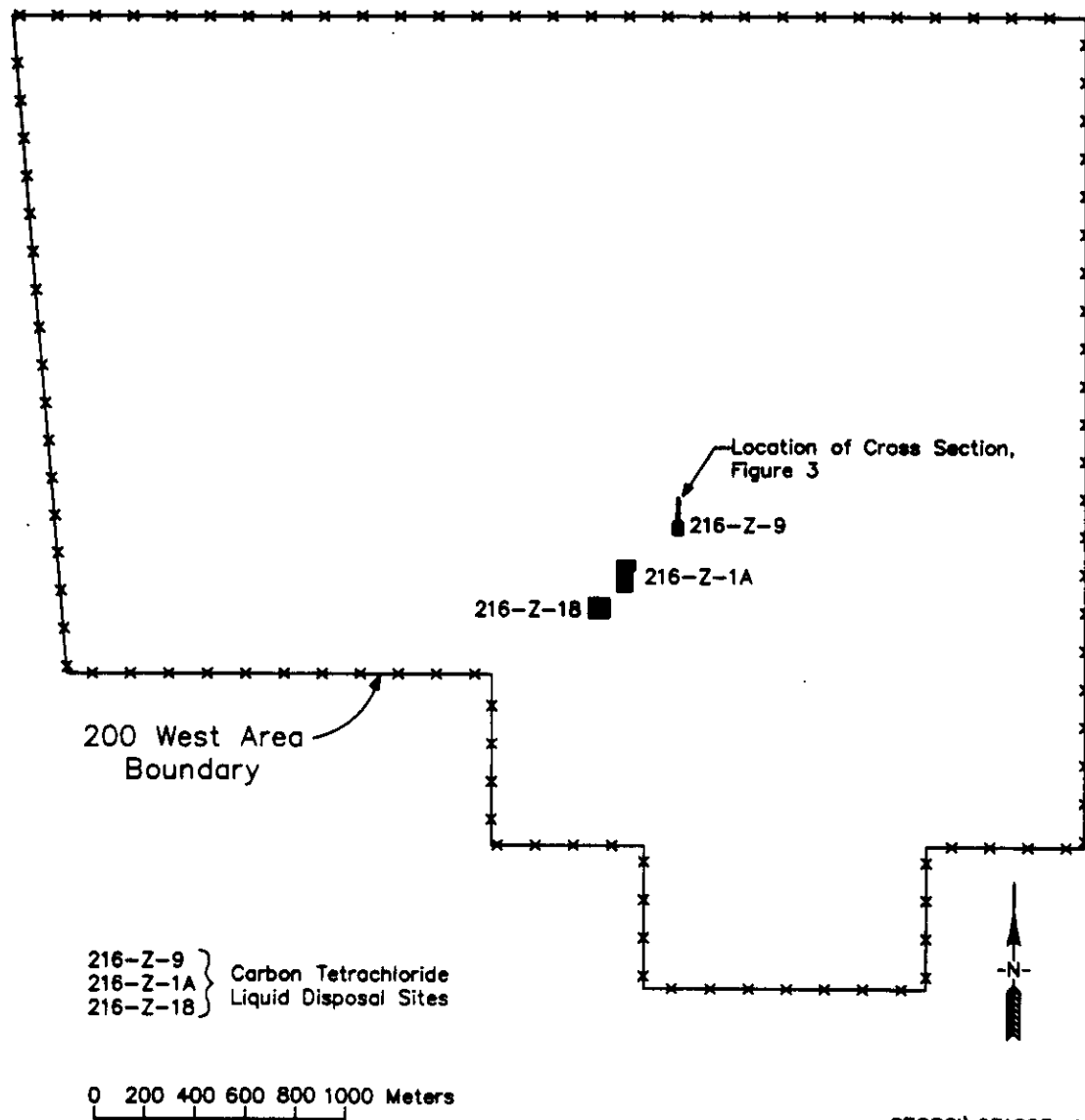
Figure 2. Annual Rates of Water and Carbon Tetrachloride
Discharged to the 216-Z-9 Trench.
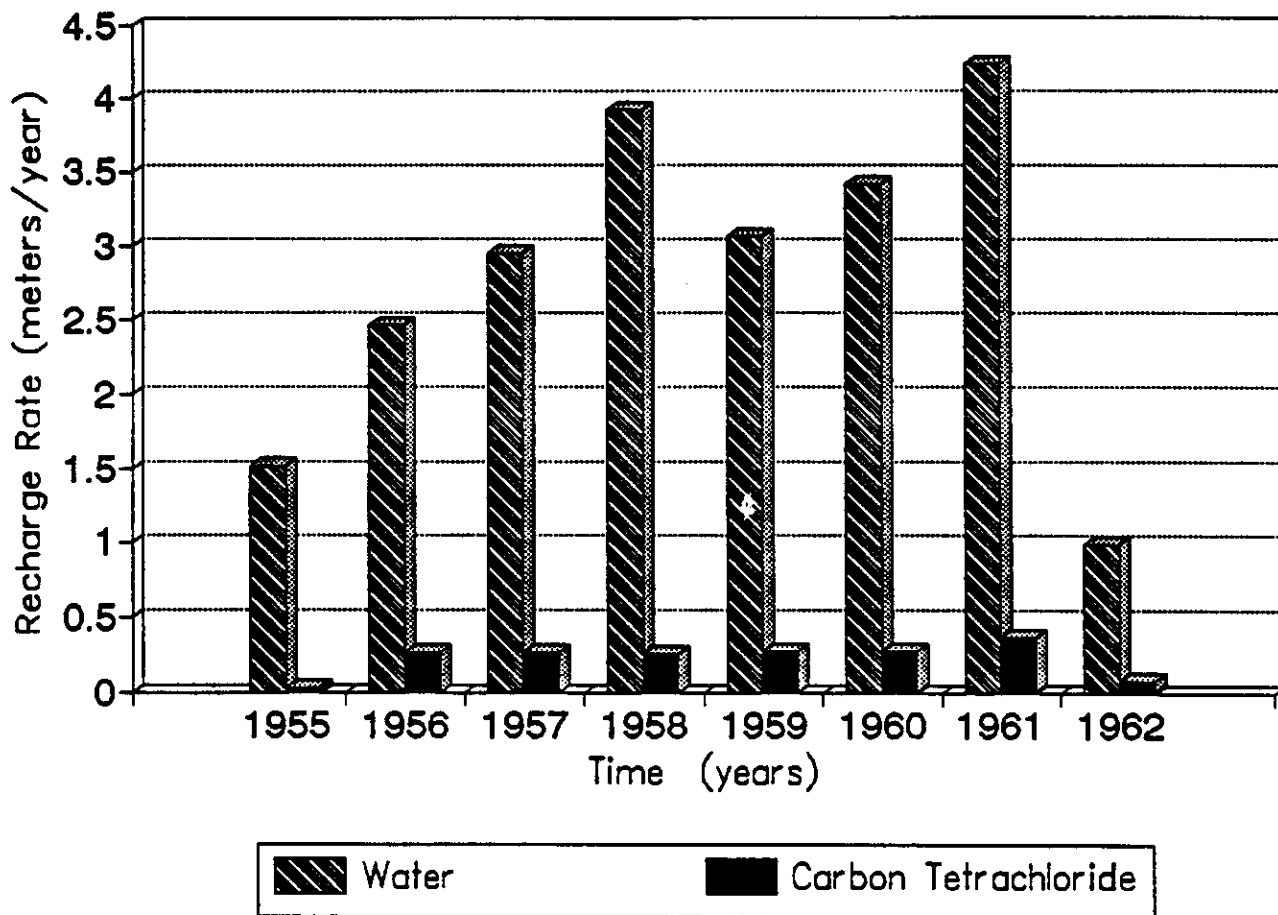
multi-phase flow of water and CCl_4, with the CCl_4 having the potential to occur as a liquid either in a "pure phase" and/or dissolved in water, as a gas, or sorbed on sediments. Gaseous CCl_4 is heavier than air so there is the potential for density-driven vapor flow.

This section will briefly discuss the fluid-media properties that influence the physical and chemical processes involved in the migration of CCl_4. A DNAPL disposed to the soil column must travel through the vadose zone (sometimes referred to as the unsaturated zone or partially saturated zone), which is about 60 m thick beneath the disposal sites in the 200 West Area, before it would reach the water table.

The transport of a DNAPL in the subsurface depends on a number of properties, such as saturation, interfacial tension, wettability, capillary pressure, residual saturation, relative permeability, solubility, volatilization, density, viscosity, and spreading. A brief discussion of these properties will provide some insight into the modeling process, which is merely a mathematical representation of the physical processes. The discussion of properties is based primarily on the paper by Mercer and Cohen (1990) supplemented with comments on spreading by Wilson et al. (1990).

Capillary pressure is a property that causes porous media to draw in the wetting fluid and repel the nonwetting fluid. Capillary pressure is a function of the interfacial tension, contact angle, and pore size. Capillary pressure affects the shape of a liquid plume in the vadose zone. Mathematically, the capillary pressure is pressure difference (total pressure) between the less wetting fluid and the more wetting fluid. For example, in a three-fluid system with water, NAPL, and air, the capillary pressure for water is $P_n - P_w$: the NAPL pressure (the non-wetting fluid) minus the water pressure (the wetting fluid). The capillary pressure for NAPL is $P_a - P_n$, the air pressure (the nonwetting fluid) minus the NAPL pressure (the wetting fluid when considering air and NAPL).

Density is the mass per unit volume of a substance. According to Mackay et al. (1985), density differences of about 1% influence the movement of fluids in the subsurface. For a DNAPL, movement below the water table will be impeded by capillary and/or permeability barriers upon which DNAPL may flow. The permeability barrier may even result in the DNAPL flowing downdip and counter to the hydraulic gradient of the ground water.

Liquid interfacial tension results from the difference between the mutual attraction of like molecules within each fluid and the attraction of dissimilar molecules across the fluid interface. It is directly related to the capillary pressure across a NAPL-water interface and is a factor controlling the wettability. The interfacial tension between a liquid and its own vapor is called vapor tension or surface tension.

Relative permeability accounts for the reduction in mobility of each of one or more fluids when they are competing for the same pore space. Relative permeability is defined as the ratio of the effective permeability of a fluid at a fixed saturation to the intrinsic permeability, and it varies from zero to one. At residual saturation of a fluid, the relative permeability becomes zero indicating that flow of that fluid ceases to occur.

Residual saturation of a DNAPL is the saturation at which the DNAPL becomes discontinuous and is immobilized by capillary forces (and the discontinuous DNAPL pathway) under ambient conditions in the vadose zone or ground water. The residual saturation results from capillary forces and depends on several factors, including the pore size distribution of the geologic media, wettability, fluid viscosity ratio and density ratio, interfacial tension, gravity/buoyancy forces, the hydraulic gradient, and spreading. Dissolution and volatilization cause the residual saturation to decrease with time.

The **saturation** of a fluid is the volume fraction of the total void volume occupied by that fluid. Saturation is important because other properties, such as capillary pressure and relative permeability, are expressed as functions of saturation.

Spreading (Wilson et al. 1990) is the phenomenon in which an organic liquid forms a film along a water-gas interface in the vadose zone. A non-spreading organic liquid does not form a film, but rather coalesces into small lenses that are held by interfacial tension at the water-gas interface. Wilson et al. (1990, p. 196) indicate that CCl_4 is a non-spreading organic and therefore will not spread as a film but tends to coalesce into lenses on the water-air interface. Wilson et al. (1990, p. 16) further suggest that soil

venting of non-spreading organics in the vadose zone may not be nearly so attractive for a remediation strategy due to the reduction of the surface area of CCl_4 resulting from coalescence.

The aqueous **solubility** of a chemical is the maximum concentration of the chemical that will dissolve in pure water at a particular temperature. Field measurements reported in the literature (Mackay et al. 1985) suggest that concentrations of organic compounds commonly occur in ground water at values less than 10% of NAPL solubility limits. DNAPL at residual saturation or in free-phase serves as a source for dissolution of that compound into ground water.

Viscosity is the internal friction within a fluid that causes it to resist flow. A compound of low viscosity will penetrate more rapidly into a soil that one with higher viscosity. When a fluid in a porous medium is displaced by another fluid, the interface between them may become unstable. This phenomenon is known as fingering and is influenced by viscosity differences between the two fluids and heterogeneities.

Volatilization refers to the transfer of matter from liquid and soil to the gaseous phase. Therefore, chemicals in the soil gas may indicate the presence of NAPL or dissolved chemicals. Volatilization is affected by vapor pressure and solubility. Once a chemical volatilizes and becomes part of the gas phase, it is transported and ultimately condenses, is sorbed onto soil particles, degraded, or is released to the atmosphere. Volatilization also represents a source for vapor transport. Density-driven gas flow, which occurs when the density of the gas is greater than that of air, can be an important transport mechanism in the vadose zone that may result in contamination of the underlying ground water by diffusion and significant dissipation of residual NAPL (Falta et al. 1989). The density of gaseous CCl_4 is greater than the density of air.

The **wettability** describes the preferential spreading of one fluid over a solid surface and other fluids in a multi-fluid system, and is a function of the interfacial tensions. The wetting fluid will tend to coat the surface of grains and occupy smaller spaces (pore throats) in the porous media, and the nonwetting fluid will tend to be constricted to the largest pores. A measure of the wettability is the contact angle. If the contact angle is <70° the system is water-wet; if the contact angle is >110° the system is NAPL-wet. For contact angles between 70° and 110° the system is neutral. For the application at the Hanford Site, existing information suggests that the system is water-wet.

2.0 VADOSE ZONE FLOW MODELING

This chapter provides a discussion of the modeling that has been performed for predicting the movement of water and CCl_4 in the vadose zone. The overall approach was to first treat the problem as only single-phase flow of water in order to obtain a basic understanding of the geohydrologic system and the interaction of the disposed effluent with this system. This also provides an indication of how the model will perform when addressing multi-phase flow. Subsequently, a two-phase approach was undertaken with the

effluent considered to be composed of both water and CCl_4. However, it was found that the computer code being used ran faster when three phases were simulated: water, liquid CCl_4, and air.

The PORFLOW computer code (Runchal and Sagar 1991) was chosen initially based on a review of existing capabilities. The PORFLOW code was adequate for the investigation of single-phase flow, although after several model runs it was deemed expeditious to concentrate the modeling effort on one site. The 216-Z-9 Trench was selected as it received the most CCl_4 on a unit area basis. Later when the two-phase flow situation was investigated, the PORFLOW code required an excessive amount of computer time for the simulation, so the SAMFT2D code was selected to model multi-phase flow.

The conceptual model of the 216-Z-9 Trench site and the immiscible fluid flow is discussed in the next subsection. The ideas and picture introduced in the conceptual model are then addressed in subsections dealing with single-phase and multi-phase flow.

2.1 CONCEPTUAL MODEL

The modeling process begins with development of a "picture" of the problem based on known information, including descriptions of the source term, the disposal facility, geologic environment and its hydrologic properties, and the pertinent properties of the organic compound of interest.

For the numerical model to predict the movement of water into the vadose zone, an accounting of the fluids introduced into the trench must be established. The 216-Z-9 Trench operated from 1955-1962 and is estimated to have received the volumes of water and CCl_4 listed in Table 1. A graphical representation of the volumes of water and CCl_4 discharged to the 216-Z-9 Trench is shown in Figure 2.

The major lithologic units that lie above the water table beneath the 216-Z-9 Trench are, in descending order, the Hanford formation, the Early Palouse soil, the Plio-Pleistocene unit (often referred to as "caliche"), and the unsaturated portion of the Ringold Fluvial Sequence E (FSE), often referred to as the Middle Ringold Formation. The Hanford formation, deposited as a result of cataclysmic flood waters, is composed of glaciofluvial gravels, sands, and silts. The Early Palouse soil consists of eolian silt and fined-grained sand. The Plio-Pleistocene consists of basaltic detritus and a carbonate-rich paleosol. The FSE is a series of alluvial gravels and sands, overbank deposits, and lacustrine deposits. Additional information on the geology may be obtained from DOE-RL (1991). Detailed information on the surfaces of these geologic units in the vicinity of the 216-Z-9 Trench was obtained from data collected in this ERA investigation as noted in the project plan (Hagood and Rohay 1991), and from other reports and maps prepared by the Geosciences Group. Figure 3 is a representation of the lithology that was used in the two-dimensional numerical simulation of the 216-Z-9 Trench. The location of this cross section is indicated by the north-south line extending from the crib in Figure 1. This cross section is 100 m long and extends from ground surface to the water table (approximately 60 m).

Table 1. Volumes of Effluents Discharged to the 216-Z-9 Trench.

Year	Total liquid discharged (m^3)	Water discharged (m^3)	CCl$_4$ discharged (m^3)	Recharge of H$_2$O* ($m^3/m^2/yr$)	Recharge of CCl$_4$ ($m^3/m^2/yr$)
1955	260.00	254.88	5.12	1.52	0.031
1956	460.00	413.60	46.40	2.47	0.277
1957	540.00	493.60	46.40	2.95	0.277
1958	700.00	655.80	44.20	3.92	0.264
1959	560.00	512.70	47.30	3.07	0.283
1960	620.00	572.20	47.80	3.42	0.286
1961	770.00	706.63	63.37	4.23	0.379
1962	180.00	165.19	14.81	0.99	0.089
Sums:	4,090.00	3,774.60	315.40		

*Annual recharge (either water or CCl$_4$) was calculated by dividing the annual discharge (for either water or CCl$_4$) by the area of the trench: length of 18.288 m by width of 9.144 m = area of 167.23 m^2.

2.2 SINGLE-PHASE FLOW OF WATER

In the modeling of single-phase flow, the effluent discharged to the crib was considered to consist of only water, i.e., it was assumed that there was no CCl$_4$. The purpose was to obtain a basic understanding of the geohydrologic system and its response to the disposal of effluent to the crib. In effect this established a quasi-baseline for comparison purposes when performing the multi-phase modeling.

The numerical single-phase flow model requires data on the hydraulic properties of the geologic units. These data take the form of curves of (1) capillary pressure as a function of moisture content and (2) relative hydraulic conductivity as a function of saturation, which are referred to collectively as the "moisture characteristic curves." These curves are sometimes termed "constitutive relationships." The relationships for single-phase flow are established by laboratory analyses of sediment samples, with the results then described mathematically by a parametric model. Different curves are obtained when the samples are analyzed in the laboratory under wetting conditions (imbibition) than under drying conditions (drainage). The van Genuchten model (van Genuchten 1978) applies to the relationship between capillary pressure and moisture content, while the Mualem model (Mualem 1976) applies to the relative hydraulic conductivity curve. An alternative to the van Genuchten model is that of Brooks and Corey (1964).

The preliminary van Genuchten parameters for the geologic units are listed in Table 2 for both wetting and drying conditions. These parameters were updated later when performing the multi-phase modeling. Hence, most of the single-phase and multi-phase parameters are different quantitatively, but qualitatively they are still similar. The Mualem parameters are derived from those of van Genuchten, and the computer program, retention curve or RETC (van Genuchten et al. 1991), is used to estimate the parameters of the

Figure 3. Cross Section Showing the Lithology Underlying
the 216-Z-9 Trench.
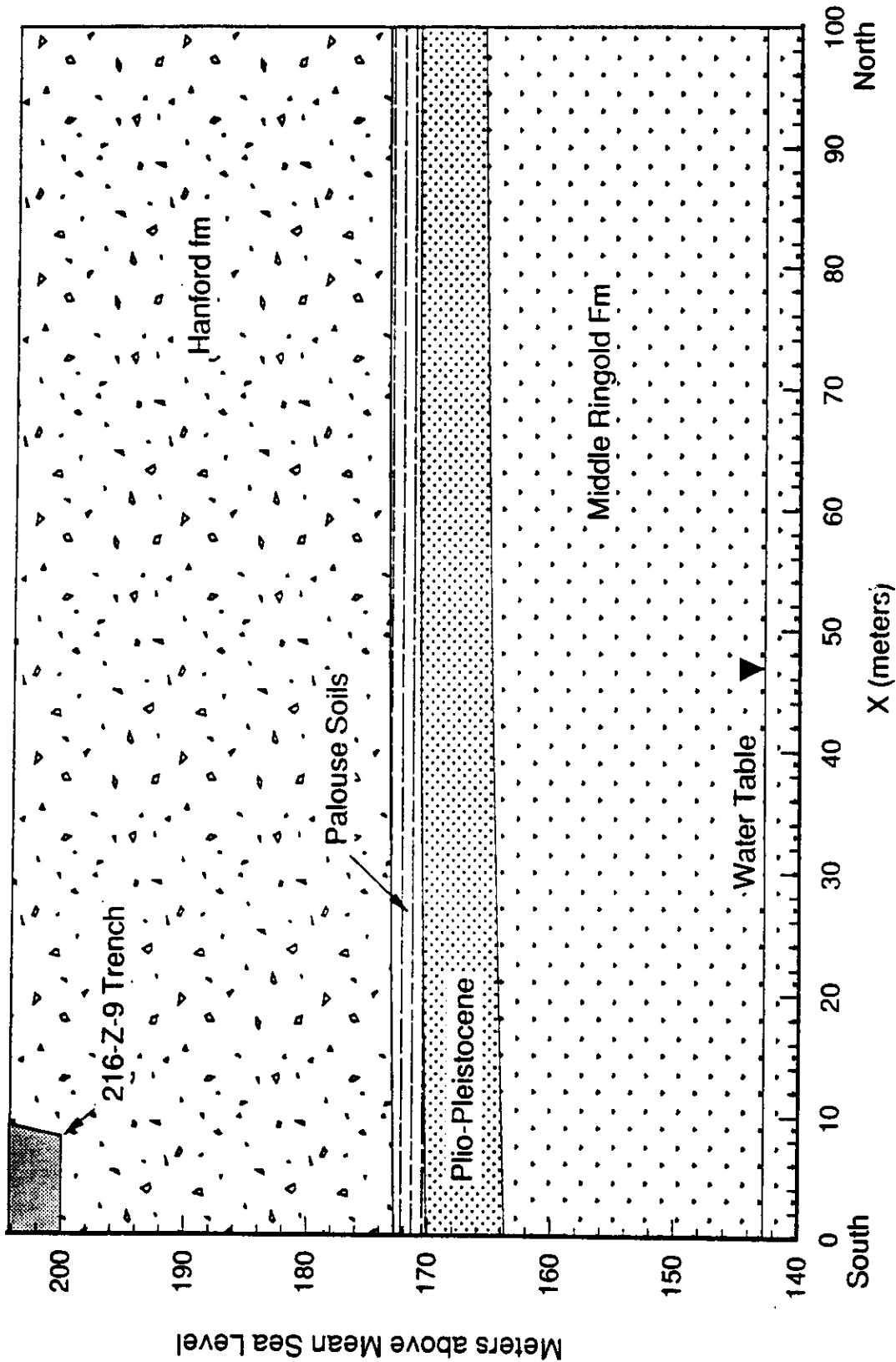
Table 2. Single-Phase van Genuchten Parameters.

Parameter	Hanford formation	Palouse Soils	Plio-Pleistocene	Middle Ringold
A. Wetting Curves				
θ_r	0.0	0.0517	0.0505	0.0342
θ_s	0.189	0.4058	0.2444	0.2507
α	0.0264	0.0105	0.1614	0.0857
n	1.222	3.0633	1.5540	1.640
B. Drying Curves				
θ_r	0.0	0.0632	0.0451	0.0268
θ_s	0.3363	0.4745	0.3565	0.3738
α	0.1714	0.0060	0.0199	0.1297
n	1.2256	3.9281	1.5140	1.551

NOTES: θ_r = residual volumetric water content (cm^3/cm^3)
θ_s = saturated volumetric water content (cm^3/cm^3)
α = van Genuchten curve-fitting parameter (cm^{-1})
n = van Genuchten curve-fitting parameter (dimensionless).

constitutive relations and to plot the constitutive relationship curves.
The preliminary moisture characteristic curves for each of the geohydrologic
units of interest, shown graphically in Figures 4 through 7, were developed
from sediment samples obtained from well 299-W7-5. This well, on the northern
edge of 200 West Area, is the well nearest the 216-Z-9 Trench for which
moisture curve data is available. This well is considered to have
geohydrologic properties that are similar to those in the vicinity of the
crib.

For the single-phase numerical simulation, the wetting curve parameters
were used since this is primarily a wetting phenomena. However, it should be
pointed out that when water retention data were measured in the laboratory,
the samples were not made wet from the irreducible saturation (the lowest
possible saturation). Therefore, the wetting curves realistically do not
represent the main wetting curve, but rather secondary wetting curves.

Other hydraulic data needed for modeling are the porosity and hydraulic
conductivity, as listed in Table 3. Again, the parameter values used for
single-phase flow were preliminary and were updated for the multi-phase flow
which was simulated later.

2.2.1 Numerical Simulations - PORFLOW Code

The PORFLOW code was a strong candidate for performing the numerical
simulation because it had been used extensively at the Hanford Site for
modeling the flow of water in the vadose zone and ground water. An enhanced
version 2.34 of PORFLOW (Runchal and Sagar 1991) had also been applied
successfully to an experiment dealing with the flow of water and oil through
sand, as described in Piepho and Runchal (1991) [oil is a light, non-aqueous

Hanford formation (coarse)
Well 299-W7-5, 11 ft Depth, Sample 0-070-4

Van Genuchten Curve Fitting
Parameters using Mualem

θ_{sw} = 0.1890
θ_r = 0.000
α_w = 0.0265 1/cm
n = 1.2220

K_{sw} = 1.20E-02 cm/s

Figure 4. Moisture Characteristic Curves for Hanford Formation: Wetting Condition.

WHC-SD-EN-TI-112, Rev. 0

11
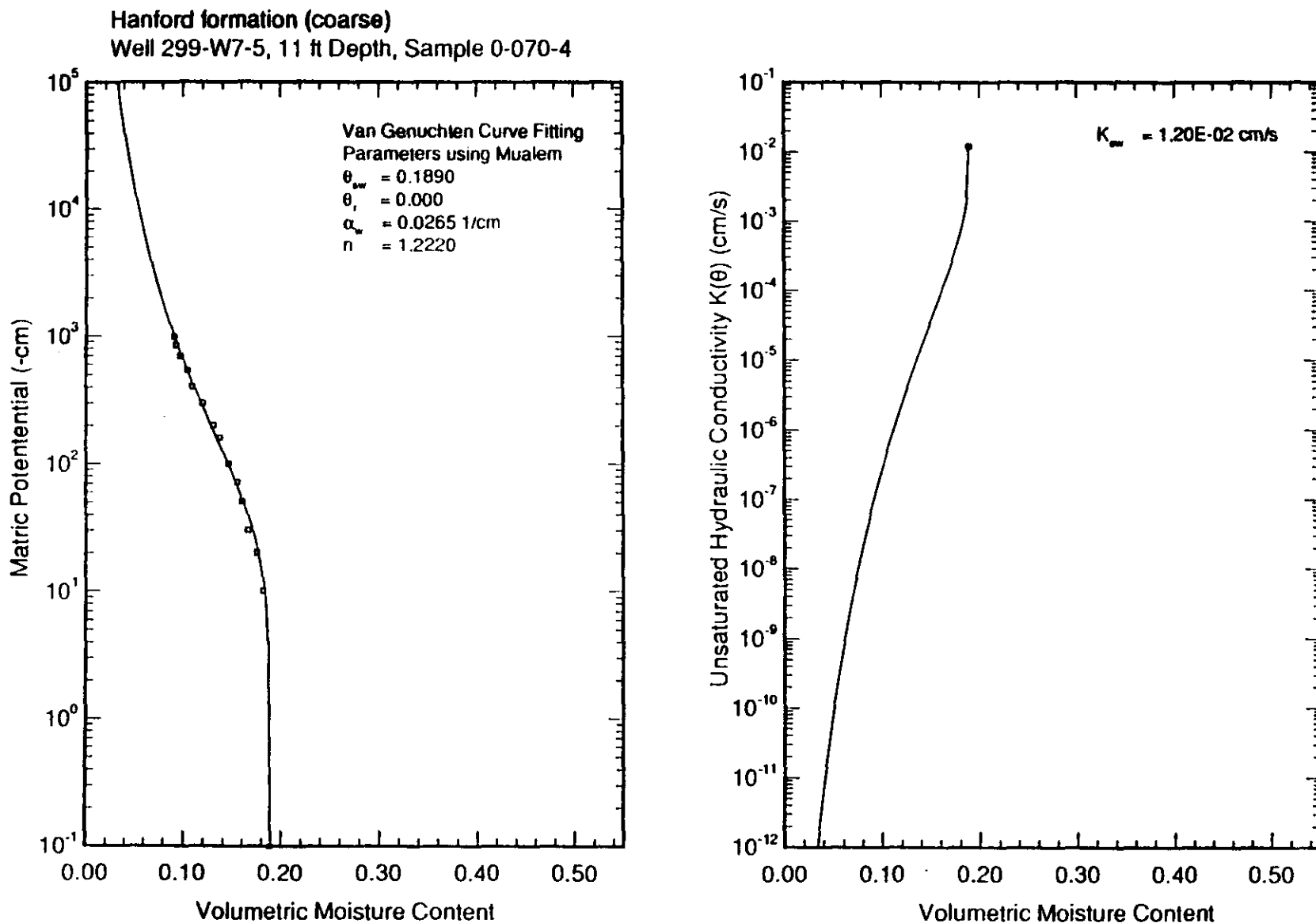
Early Palouse Soils
Well 299-W7-5, 71 ft Depth, Sample 0-080

Van Genuchten Curve Fitting
Parameters using Mualem

θ_{sw} = 0.4050
θ_r = 0.051
α_w = 0.0105 1/cm
n = 3.0633

K_{sw} = 1.40E-04 cm/s
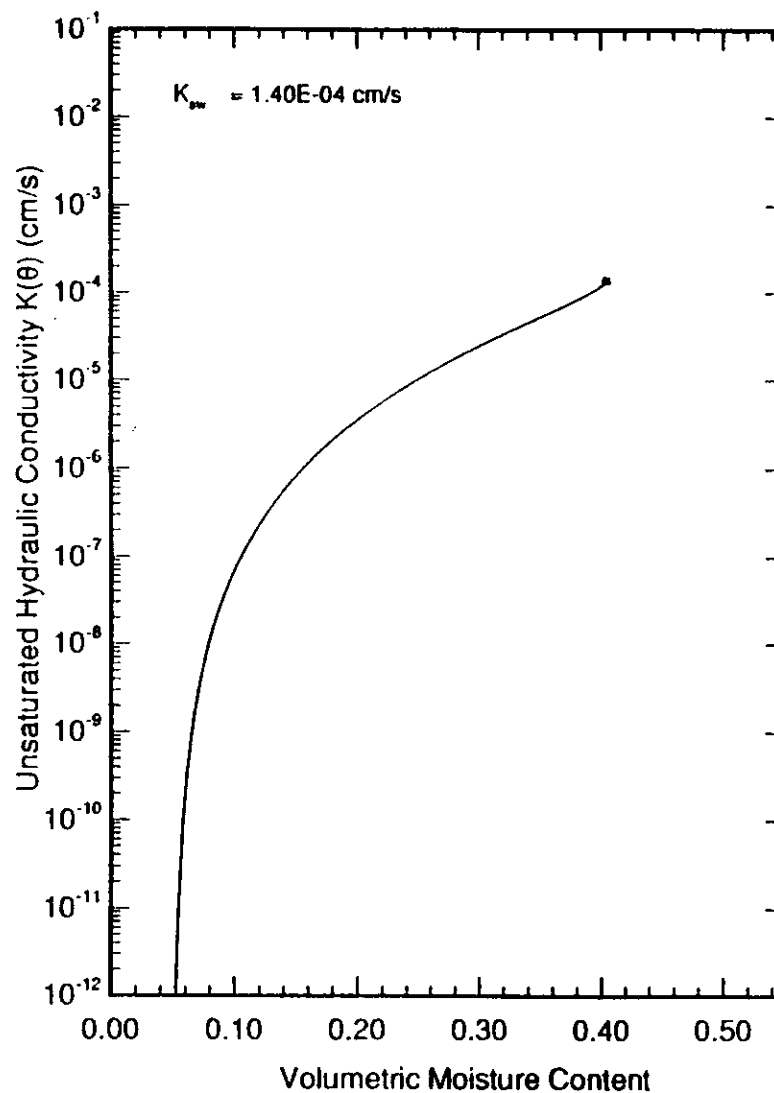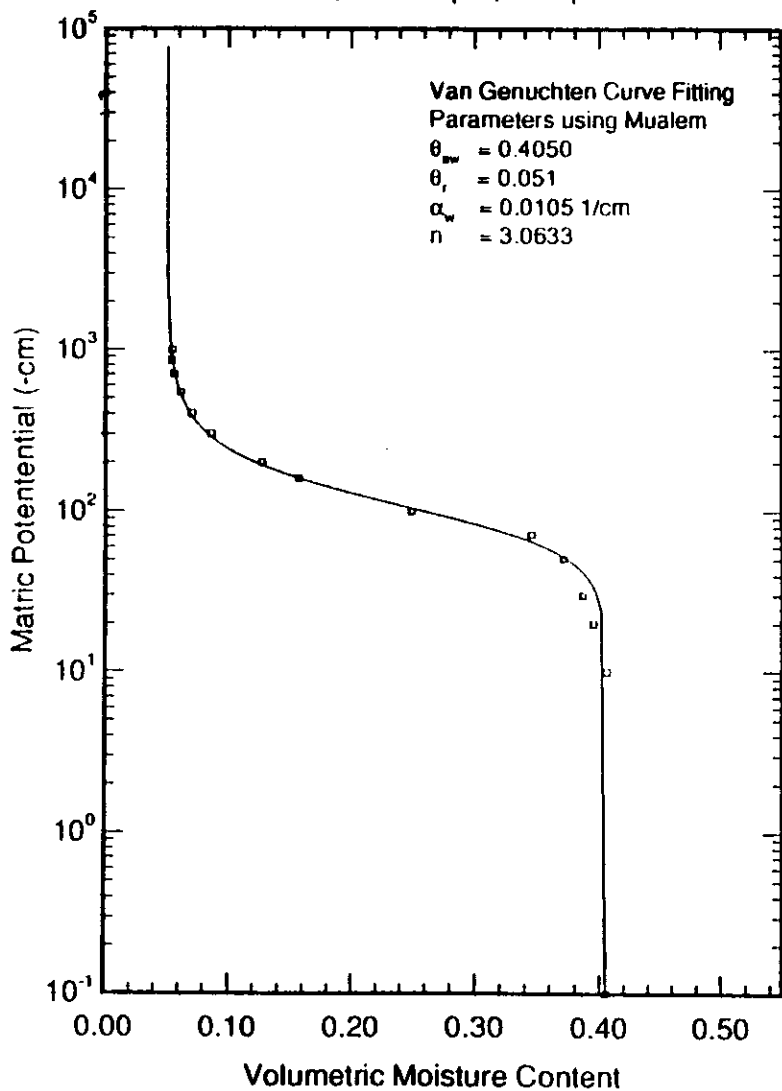
Figure 5. Moisture Characteristic Curves for Early Palouse Soils: Wetting Condition.

Plio-Pleistocene
Well 299-W7-5, 105 ft Depth, Sample 0-102

Van Genuchten Curve Fitting
Parameters using Mualem
$\theta_{sw} = 0.2444$
$\theta_r = 0.051$
$\alpha_w = 0.1614$ 1/cm
$n = 1.5540$

$K_{sw} = 2.10E\text{-}04$ cm/s
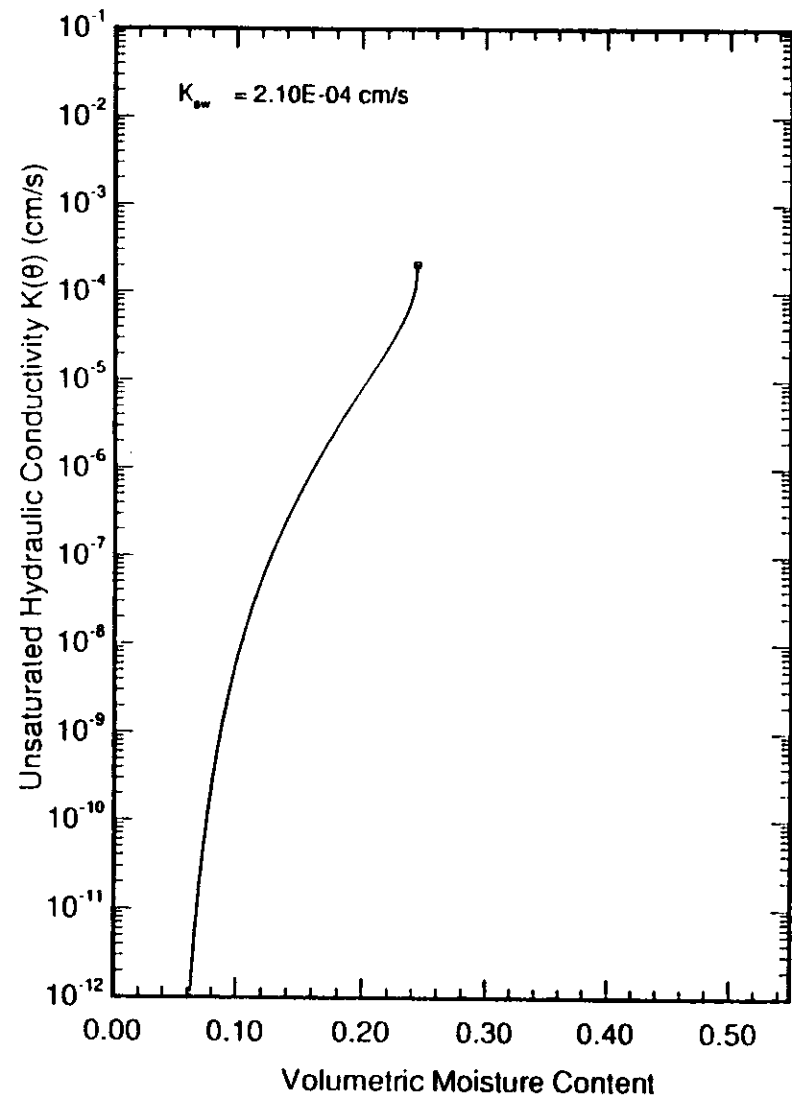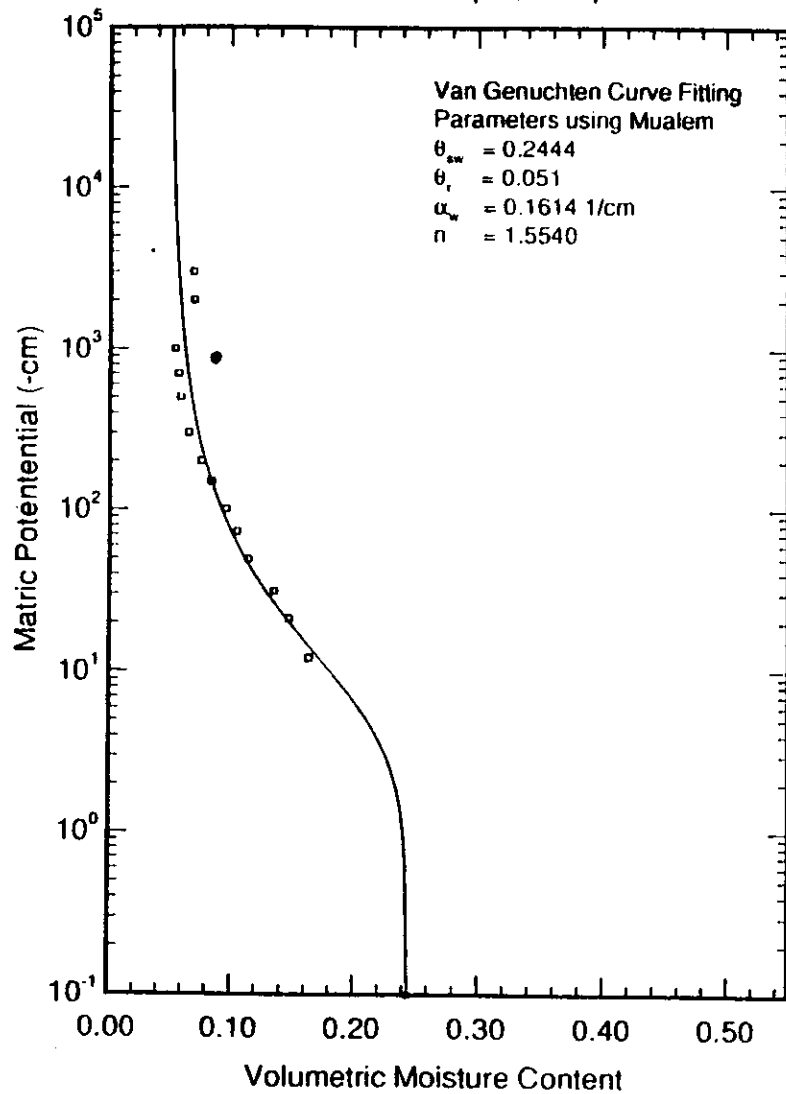
Figure 6. Moisture Characteristic Curves for Plio-Pleistocene Unit: Wetting Condition.

WHC-SD-EN-TI-112, Rev. 0

13

Middle Ringold Unit
Well 299-W7-5, 134 ft Depth, Sample 0-108

Van Genuchten Curve Fitting
Parameters using Mualem
θ_{sw} = 0.2510
θ_r = 0.034
α_w = 0.0857 1/cm
n = 1.6400

K_{sw} = 3.00E-04 cm/s
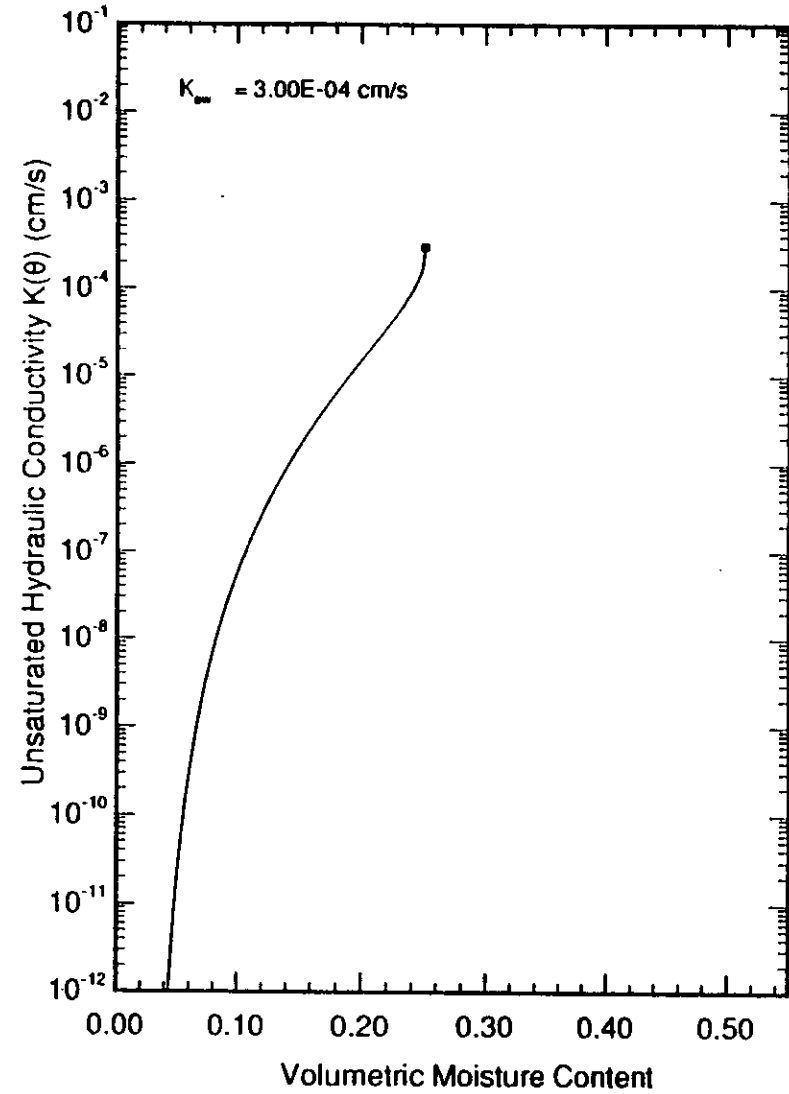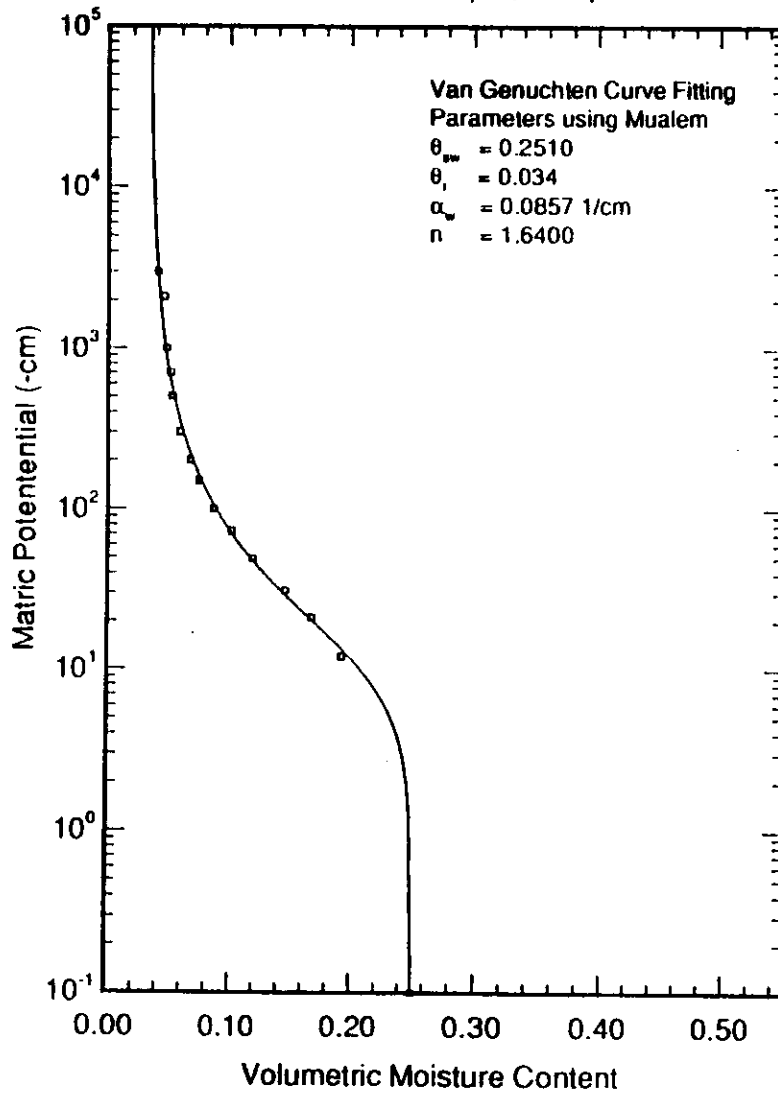
Figure 7. Moisture Characteristic Curves for Middle Ringold Formation: Wetting Condition.

WHC-SD-EN-TI-112, Rev. 0

Table 3. Saturated Hydraulic Conductivity (Ksat)
and Effective Porosity.

Parameter	Hanford formation	Palouse soils	Plio-Pleistocene	Middle Ringold
Ksat (cm/s)	1.2E-2	1.4E-4	2.1E-4	3.0E-4
Ksat (m/yr)	3.8E+3	4.4E+1	6.6E+1	9.5E+1
Effective porosity - wetting curves (cm^3/cm^3)	0.3414	0.50	0.3638	0.3759

phase liquid (LNAPL)]. The enhancements for version 2.34 included replacement of the Picard iteration scheme in the numerical solution with a modified Picard method that not only provided more accurate results but reduced the computation time by more than two orders of magnitude. For these reasons the PORFLOW code, version 2.34, was chosen for initial application of both single-phase and multi-phase flow in this ERA investigation.

The numerical simulations were performed using a two-dimensional cartesion finite-difference grid (Figure 8) containing 10,153 cells (71 in the X-axis direction and 143 in the Y-axis direction). Variable grid spacing was used in the x-direction close to the source term and in the y-direction within the Plio-Pleistocene unit and just above the water table. Near these features the grid is fine, and away from these features the grid becomes coarse. This was done to accommodate the relatively large pressure gradients close to and within these features. One distinguishing feature shown in Figure 8 is the placement of the source term below the top boundary in order to include the depth of the trench in the simulations.

Boundary and initial conditions for saturation are shown in Figure 9. The boundary conditions consisted of the water table at the bottom (i.e., the pressure head is set to 0), no flux boundaries on the left and right side of the model, and a constant recharge of 5 cm/year at the top boundary. The initial conditions at the start of the simulation were set by running the model until the discharge at the bottom boundary was equal to the recharge at the top boundary. This meant the Darcy velocity throughout the domain was equal to 5 cm/year in a downward direction (Figure 10a). Additionally, two simulations were run to assess the effects of anisotropy. The first simulation was isotropic, i.e., the hydraulic conductivities in the x and y directions were the same. In the second simulation the y-direction hydraulic conductivity was 10 times less than that in the x-direction. The initial saturations for the anisotropic model were adjusted to account for a lower y-direction hydraulic conductivity (Figure 10b).

2.2.2 Single-Phase Results

Given the source term, initial conditions, boundary conditions, and the parameters to describe the system, the model was run for the 8-year operational history of the trench. The mass balance error was calculated for each time step and was found to be within 1%. To show the movement of the wetting front through the vadose zone, Figures 11 through 13 portray the saturations at the end of each year for the isotropic case (upper plot) and anisotropic case (lower plot). Notation on each plot indicates the year of

Figure 8. Finite Difference Grid Used in Numerical Simulation of Liquid Effluent from 216-Z-9 Trench.
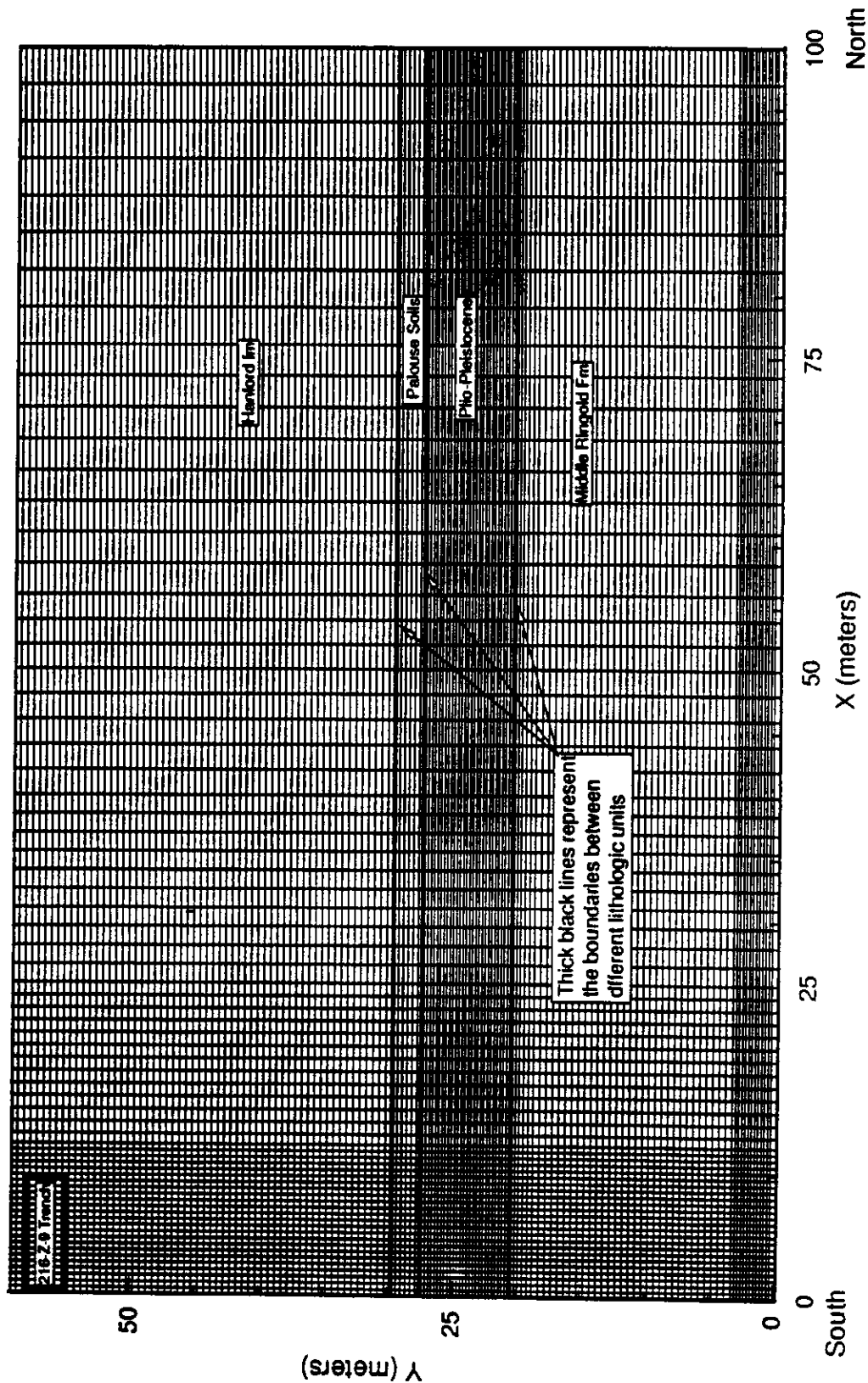
Figure 9.   Initial and Boundary Conditions Used in the Single-
Phase (Water) Numerical Simulation of Liquid Effluent
from the 216-Z-9 Trench (Darcy Velocity).
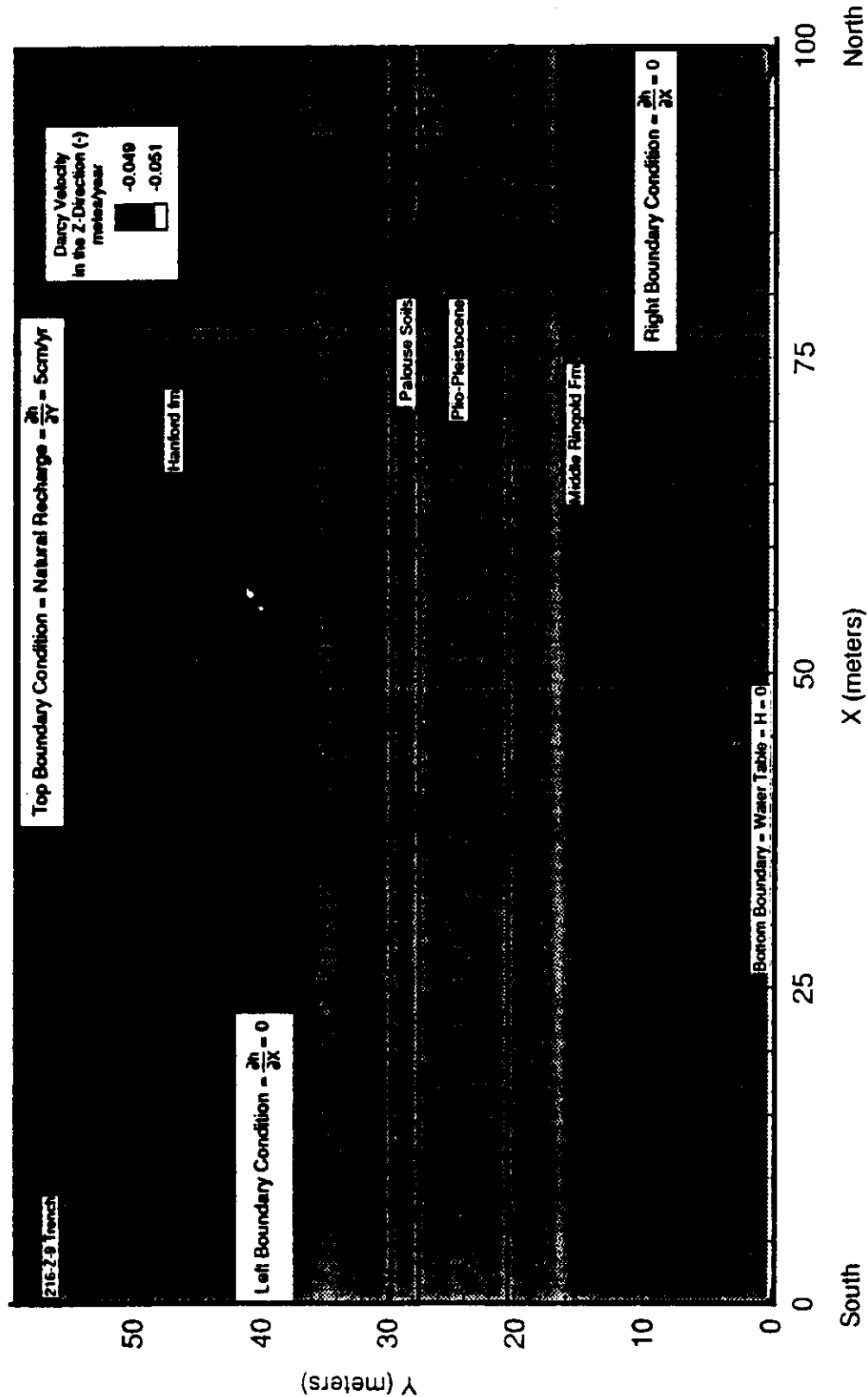
Figure 10. Initial and Boundary Conditions Used in the Single-Phase (Water) Simulation of Liquid Effluent from the 216-Z-9 Trench (Saturations): Part A - Isotropic, Part B - Anisotropic.
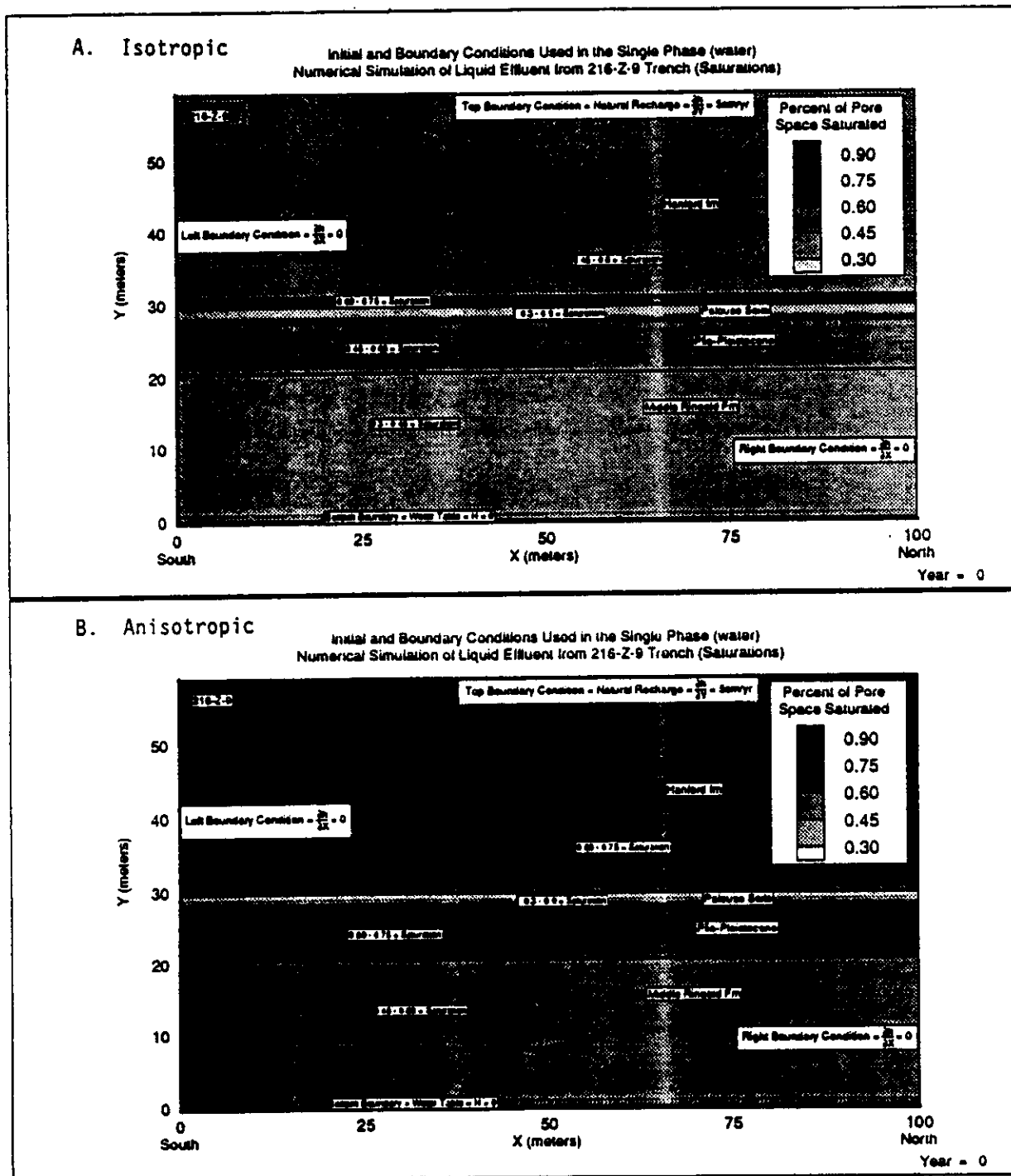
**Figure 11. Simulated Distribution of Moisture at End of Year 1:
Part A - Isotropic, Part B - Anisotropic.**
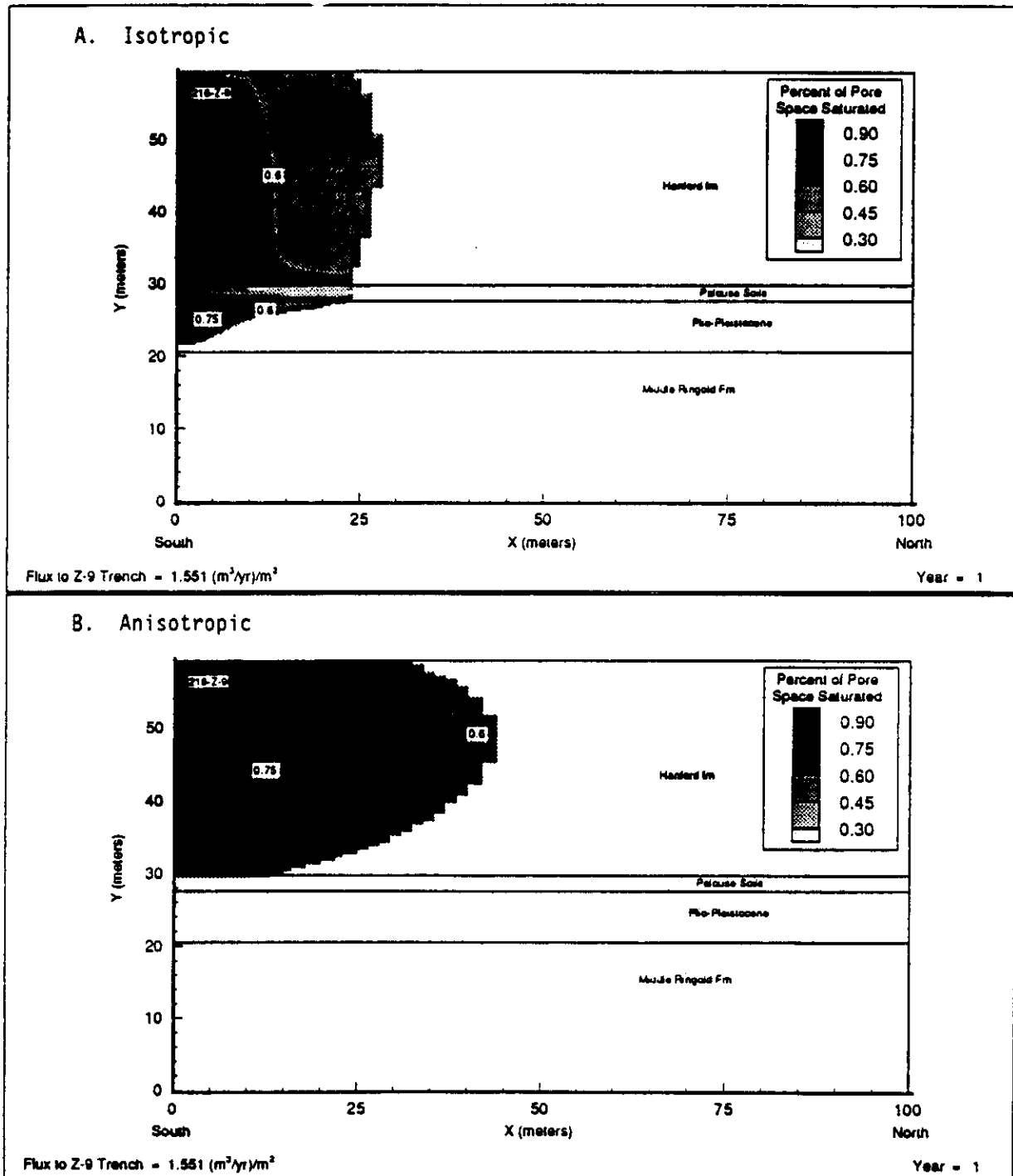
Figure 12.   Simulated Distribution of Moisture at End of Year 2: Part A - Isotropic, Part B - Anisotropic.
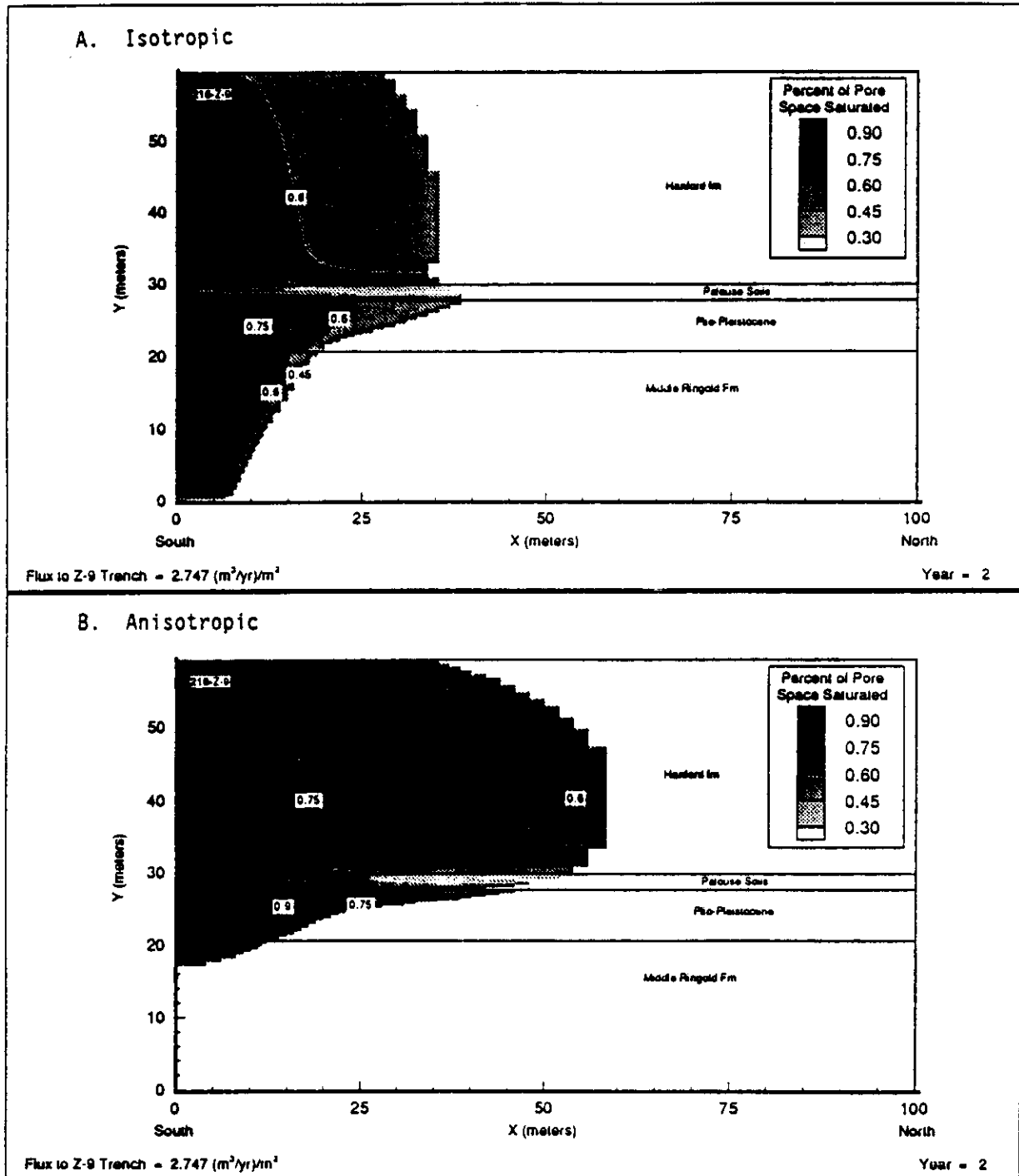
Figure 13.   Simulated Distribution of Moisture at End of Year 3:
Part A - Isotropic, Part B - Anisotropic.
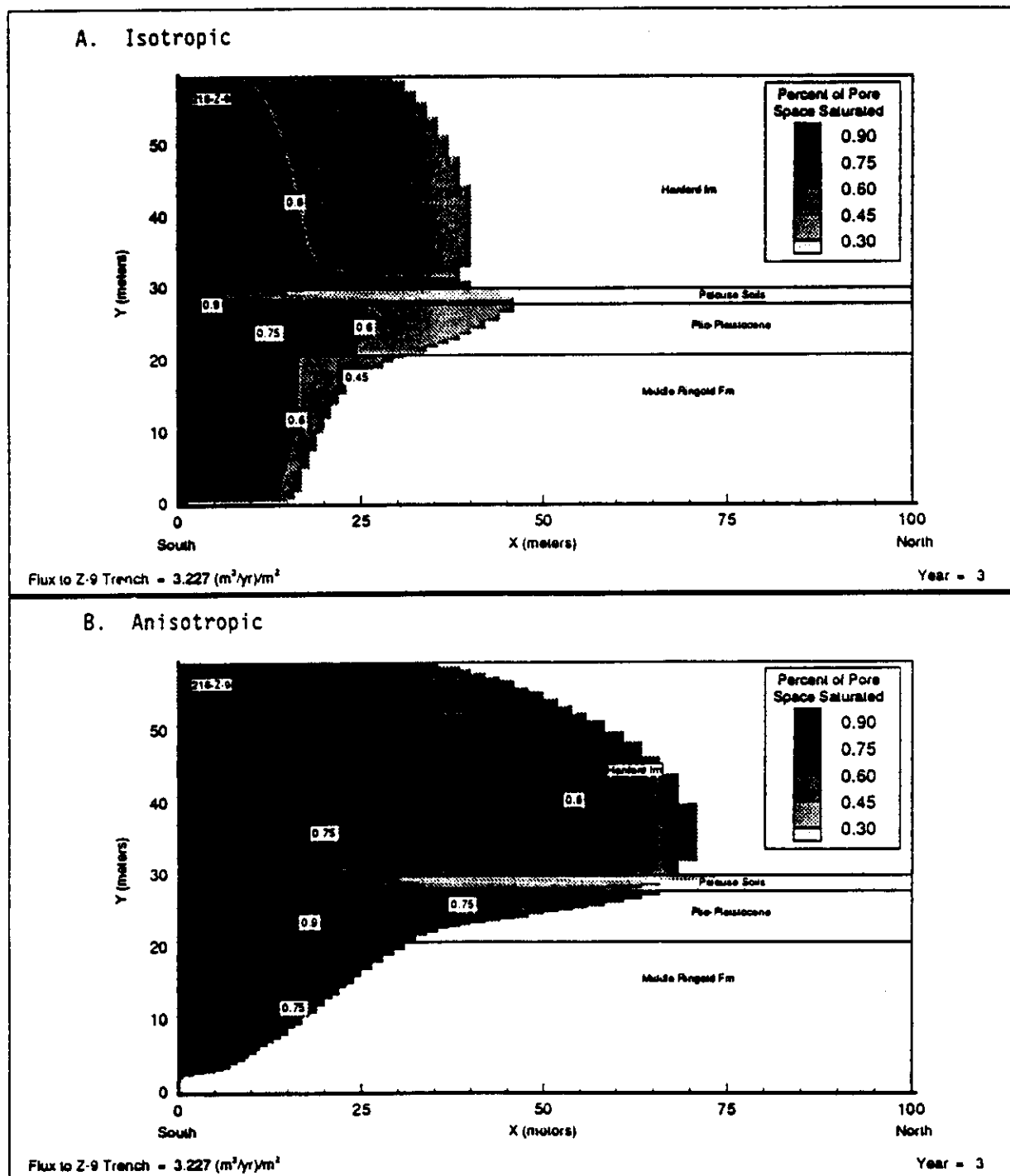
the simulation and the discharge to the trench during that year. In these figures only the finite difference nodes with a change in saturation greater than 0.1% over the initial conditions are plotted.

The wetting front under isotropic conditions propagates through the upper two layers and most of the third (Figures 11a and 12a) in less than a year and reaches the water table in approximately 1.9 years. In contrast to this, the wetting front under anisotropic conditions reaches the ground-water table in 3.2 years (Figures 11b through 13b). This illustrates the nonlinearity of the unsaturated flow problem. Although the wetting front for the anisotropic case arrived at the water table by a factor of 1.68 behind the isotropic case, the y-direction saturated hydraulic conductivity had been decreased by a factor of 10. For the anisotropic case to pass the same amount of water as the isotropic case, the saturations have to be larger. With larger saturations the relative hydraulic conductivity becomes larger.

Lateral spreading of the moisture front can clearly be seen in both the isotropic and anisotropic cases. However, it is clearly more pronounced in the anisotropic case. To quantify the difference between the cases, the volume of water passing through the model was calculated at each time step. A summary of these calculations for mass entering, leaving, and accumulating in the model for each year of the simulation is given in Table 4.

In summary, a two-dimensional numerical model was constructed with PORFLOW code to simulate water flow (single-phase flow) from the 216-Z-9 Trench through the vadose zone to the water table. The primary objectives of this model were to:

- Determine the amount of lateral spreading for both isotropic and anisotropic conditions

- Estimate the amount of water remaining in the vadose zone and the flux to the water table.

For the isotropic case, water flow is essentially one-dimensional with all but 15% of the mass introduced passing through the system at the end of eight years. While for the anisotropic case, water flow is multidimensional with 38% of the mass introduced remaining in the vadose zone. This contaminated water remaining in the vadose zone could become a source for CCl_4 vapors by partitioning between water soluble CCl_4 and air according to Henry's Law. It is also evident from the last year's results that water remaining in the vadose zone will continue to drain to the water table.

PORFLOW, version 2.34, calculated single-phase flow solutions with reasonable computer times and mass balances checking out well. This part was very important because it demonstrated the importance of the stratigraphy and confirmed the appropriateness of the preliminary hydraulic parameters for unsaturated flow. In particular, it was noted that the lower hydraulic conductivity of the Palouse soil layer relative to the Hanford formation causes lateral spreading of the moisture plume as it moves downward.

Table 4.   Mass Balance for the Isotropic and Anisotropic Cases.

Year	Total volume introduced during year (m^3)	Total volume in model at end of year (m^3)	Net accumulated volume in model at end of year (m^3)	Total volume discharged to water table during year (m^3)
A. Isotropic Case				
0	0.0	648.7		
1	14.3	662.9	14.3	0.0
2	25.1	686.5	23.6	-1.5
3	29.5	696.3	9.8	-19.7
4	38.3	703.8	7.4	-30.8
5	30.7	702.4	-1.4	-32.1
6	33.9	704.8	2.4	-31.5
7	42.1	709.0	4.3	-37.9
8	9.9	690.1	-19.0	-28.8
Total	223.8		32.8	-182.3
B. Anisotropic Case				
0	0.0	809.1		
1	14.3	823.4	14.3	0.0
2	22.6	846.0	22.6	0.0
3	27.0	872.9	27.0	0.0
4	38.3	897.8	24.9	-13.4
5	30.7	901.1	3.3	-27.4
6	33.9	907.3	6.2	-27.7
7	42.1	913.6	8.6	-33.5
8	9.9	891.9	-24.1	-34.0
Total	218.8		82.8	-136.0

NOTE: The "Total Volume Introduced During Year," column 2, is obtained by dividing the "Total Liquid Discharged," column 2 of Table 1, by the length of the trench, 18.288 m.   The "Total Volume in Model at End of Year," column 3, is obtained as output from the numerical model.   The difference between column 3 for any year and the preceding year is the "Net Accumulated Volume in Model at End of Year," column 4.   The "Total Volume Discharged to Water Table During Year," column 5, is obtained by subtracting column 4 from column 2.   Negative numbers in columns 4 and 5 indicate the volume that has passed through the model.   Using year 3 for the isotropic case as an example, column 2 = 540 m^3 (from Table 1, column 2, for year 3, 1957) divided by 18.288 m = 29.4 m^3; column 3 is obtained from the numerical model; column 4 = 696.3 m^3 (column 3 for year 3) - 686.5 m^3 (column 3 for year 2) = 9.8 m^3; column 5 = 29.5 m^3 (column 2) - 9.8 m^3 (column 4) = -19.7 m^3.

2.3 MULTI-PHASE FLOW OF WATER AND CARBON TETRACHLORIDE

An approach that is more realistic than dealing with water as the only fluid in the porous media system is to consider the simultaneous movement of water, liquid CCl_4, and air within the system. The simulation of this system requires the application of a code that can deal with multi-phase flow and transport.

2.3.1 Multi-Phase Constitutive Relationships and Parameters

No matter which computer code is used, the constitutive relationships discussed in Section 2.2 for single-phase flow must be extended to account for the additional one or more phases.

The van Genuchten moisture retention parameters discussed in Section 2.2 may be extended for multi-phase flow by the method presented in Lenhard and Parker (1987, 1988) to get saturations for each phase. This extension requires the computation of scaling parameters that are calculated from the ratios of interfacial tension values. The scaling parameters permit the expression of the capillary pressure-soil saturation relations for the combinations of fluid pairs (e.g., air-water, air-CCl_4, water-CCl_4) as appropriate in a given problem.

As mentioned in Section 2.2, an alternative to the van Genuchten saturation-capillary pressure function is that of Brooks and Corey (1964). The Brooks-Corey function may also be extended to multi-phase flow with the application of the scaling parameters noted in the previous paragraph (Lenhard and Parker 1987, 1988).

In addition to these capillary pressure functions, relative permeability functions for multi-phase flow are also required for simulations of multi-phase flow. Parker (1989) developed a method for extending Mualem's theory to obtain the relative permeabilities as a function of capillary pressure for multi-phase flow.

The constitutive relations referred to above had been used successfully for the transmission oil simulations reported in Piepho and Runchal (1991). However, the oil industry has been using a different technique for relative permeability functions, either the Stone-1 (Stone 1970) or Stone-2 method (Stone 1973) rather than the extended Mualem method based on either the van Genuchten or Brooks-Corey capillary functions. The Stone-2 method was selected for initial application because of extensive use in the oil industry, and upon its recommendation by HydroGeoLogic.

The Stone-2 method is an empirical curve fit that, in effect, interpolates the relative permeability of water and air from a water/air system and the relative permeability of CCl_4 and water in a water/CCl_4 system to obtain the relative permeability of CCl_4 in a three-phase system (water/CCl_4/air).

The functional relationships that were used for multi-phase flow are listed below. First, the relative permeabilities for two-phase flow using Brooks-Corey/Mualem and van Genuchten/Mualem theories are given. SAMFT2D has the option of using either of these methods for two-phase flow. Then the capillary pressure functions are given based on van Genuchten's theory, which is the theory that the SAMFT2D code uses for capillary pressures. Finally, the Stone-1 and Stone-2 methods, and the extended van Genuchten/Mualem and Brooks-Corey/Mualem theories for the NAPL relative permeability (k_{rn}) for a three-phase (water, NAPL, air) system are given. The user of SAMFT2D has the option of selecting any one of these four methods for dealing with relative permeabilities.

Two-Phase Brooks-Corey/Mualem Relative Permeabilities:

The Brooks-Corey/Mualem relative permeabilities (Honapour et al. 1986) may be stated as follows:

$$k_{rw} = \overline{S_w}^{N+2}$$

$$k_{ra} = (\overline{S_a})^2 \left[1 - (1 - \overline{S_a})^N\right]$$

$$k_{rn}^{wn} = (1 - \overline{S_w})^2 \left[1 - \overline{S_w}^N\right]$$

$$k_{rn}^{na} = (1 - \overline{S_a})^{N+2} = \overline{S_L}^{N+2}$$

$$\overline{S_w} = \frac{S_w - S_{wr}}{1 - S_w}$$

$$\overline{S_a} = \frac{S_a}{1 - S_{wr}}$$

(1)

In the above equations,

k_{rw} = relative permeability to water in an air-water system

k_{ra} = relative permeability to air in an air-water system

k_{rn}^{wn} = relative permeability to NAPL in a water-NAPL system (a function of water saturation)

k_{rn}^{na} = relative permeability to NAPL in an air-NAPL system (a function of air saturation)

$\overline{S}$ = effective wetting phase saturation, with the subscripts "w" and "a" referring to water and air, respectively

$\overline{S_L}$ = $1 - \overline{S_a}$ = effective liquid saturation (including both NAPL and water)

25

S_w = absolute water saturation

S_{wr} = residual water saturation

S_a = absolute air saturation

N = 1 + 2/mn, where the product "mn" is the Brooks-Corey pore size distribution parameter (see Table 5).

Two-Phase van Genuchten/Mualem Relative Permeabilities:

$$k_{rw} = (\overline{S_w})^{1/2} \; [1-(1-\overline{S_w}^{1/m})]^2$$

$$k_{ra} = (\overline{S_a})^{1/2} \; [1 - \overline{S_L}^{1/m}]^{2m}$$

$$k_{rn}^{wn} = (1 - \overline{S_w} - \overline{S_{nr}})^{1/2} \; (1 - \overline{S_w}^{1/m})^{2m}$$

$$k_{rn}^{na} = (1 - \overline{S_w} - \overline{S_{nr}})^{1/2} \; [1-(1- \overline{S_L}^{1/m})^m]^2$$

(2)

where the terms are as previously defined for the two-phase Brooks-Corey relative permeabilities.

van Genuchten Capillary Pressure Functions

The capillary pressure functions of van Genuchten as used in SAMFT2D are (Huyakorn et al. 1991)

$$P_{cnw} = \frac{\sigma_{nw}\rho_{fw}g}{\alpha\sigma_{aw}}[(\overline{S_w})^{-1/m}-1]^{1/n}$$

$$P_{can} = \frac{\sigma_{an}\rho_{fw}g}{\alpha\sigma_{aw}}[(1 - \overline{S_a})^{-1/m}-1]^{1/n}$$

(3)

$$P_{caw} = \frac{\rho_{fw}g}{\alpha}[(1 - \overline{S_a})^{-1/m}-1]^{1/n}$$

Table 5. Multi-Phase Parameters for Constitutive Relationships/Flow Model.

Parameter	Hanford formation	Palouse Soils	Plio-Pleistocene	Middle Ringold
A. Wetting Curves				
van Genuchten:				
S_r ($= \theta_r/\theta_s$)	0.0833	0.1350	0.0476	0.1064
Porosity, θ_s	0.2569	0.3900	0.3276	0.2520
α	0.0395	0.0078	0.0116	0.0975
n	1.660	3.0619	1.1600	1.5518
Brooks-Corey:				
mn	0.6600	2.062	0.16	0.552
N	4.0303	1.970	13.50	4.625
Ksat (vertical)	2.85E-5	7.82E-5	3.87E-5	1.02E-4
k^* (base value)	0.45	0.51	0.45	0.45
B. Drying Curves				
van Genuchten:				
S_r ($= \theta_r/\theta_s$)	0.1026	0.1098	0.0869	0.0396
Porosity, θ_s	0.3792	0.4745	0.4328	0.4140
α	0.0724	0.0054	0.0199	0.0662
n	1.60	3.0619	1.5635	1.3957
Brooks-Corey:				
mn	0.600	2.062	0.5635	0.3957
N	4.333	1.970	4.5492	6.0543
Ksat (vertical)	2.39E-3	1.4E-4	3.87E-5	2.1E-3
k^* (base value)	0.45	0.51	0.45	0.45

NOTES:
θ_r = residual volumetric water content (cm^3/cm^3)
θ_s = saturated volumetric water content (cm^3/cm^3)
α = van Genuchten curve-fitting parameter (cm^{-1}), and approximation to inverse bubbling pressure for Brooks-Corey fit
n = van Genuchten curve-fitting parameter (dimensionless)
m = 1 - 1/n
N = Brooks-Corey fitting parameter = 1 + 2/mn
mn = Brooks-Corey pore-size parameter = m x n
Ksat = saturated conductivity (cm/sec)
k^* = relative permeability of NAPL at irreducible water saturation.

which, upon substitution for ρ_{fw}, g and σ's become

$$P_{cnw} = \frac{605.345}{\alpha}\left[(\overline{S_w})^{-1/m}-1\right]^{1/n}$$

$$P_{can} = \frac{361.886}{\alpha}\left[(1 - \overline{S_a})^{-1/m}-1\right]^{1/n} \tag{4}$$

$$P_{caw} = \frac{980.66}{\alpha}\left[(1 - \overline{S_a})^{-1/m}-1\right]^{1/n}$$

In these equations

P_c = capillary pressure (dynes/cm^2 or pascals)

σ = interfacial tension (dynes/cm)

α = van Genuchten curve-fitting parameter (cm^{-1})

n (superscript) = van Genuchten curve-fitting parameter (dimensionless)

m = 1 - 1/n

ρ_{fw} = density of water

g = acceleration due to gravity.

$\overline{S_w}$ and $\overline{S_a}$ are the same as defined above.

In the above equations the subscripts "nw", "an", and "aw" relate to NAPL and water, air and NAPL, and air and water, respectively.

Three-Phase NAPL Relative Permeabilities:

<u>Stone-1 Method</u>

$$k_{rn} = \frac{k_{rn}^{wn}\ k_{rn}^{na}\ S_n^*}{(1 - S_w^*)(1 - S_a^*)\ k^*}$$

$$S_n^* = \frac{S_n - S_{nr}}{1 - S_{wr} - S_{nr}}$$

$$S_w^* = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}$$

$$S_a^* = \frac{S_a}{1 - S_{wr} - S_{nr}} \tag{5}$$

Where

S_n = *absolute NAPL saturation*

S_{nr} = *residual NAPL saturation*

$$k* = \frac{k^{wn}}{k_{rn}}\ at\ s_{wr}\quad (or\ S_L = 1)$$

and k_{rn}^{wn} and k_{rn}^{na} are the same as noted above

<u>Stone-2 Method</u>

$$k_{rn} = k*[(k_{rn}^{wn}/k^* + k_{rw})(k_{rn}^{na}/k^* + k_{ra}) - (k_{rw} + k_{ra})]$$

Where $\tag{6}$

$$k* = \frac{k^{wn}}{k_{rn}}\quad at\ S_w = S_{wr}\quad (or\ S_L = 1)$$

<u>van Genuchten/Mualem Extension</u>

$$k_{rn} = (\overline{S_L} - \overline{S_w} - \overline{S_{wr}})^{1/2}\ (((1 - \overline{S_w}^{1/m})^m - (1 - \overline{S_L}^{1/m})^m))^2 \tag{7}$$

Brooks-Corey/Mualem Extension

$$k_{rn} = (\overline{S_L} - \overline{S_w} - \overline{S_{wr}})^2 \ (\overline{S_L}^N - \overline{S_w}^N) \qquad (8)$$

where all terms are as previously defined.

The constitutive relations that were used in conjunction with Stone's 2 method were the Brooks-Corey relationship for saturations and two-phase relative permeabilities and the van Genuchten relationship for capillary pressure. The Brooks-Corey relationship was used to determine the two-phase relative permeabilities as a function of moisture and air content, and the van Genuchten relationship was used to determine the soil capillary pressures as a function of moisture and air content.

The draining curves were also used in some simulations even though this problem is definitely an imbibition problem. One reason for also using the draining curves was to examine the sensitivity of both of these characteristic curves. Another reason was that the wetting curves were derived primarily for the single-phase flow model and, as a result, the effective porosities and the saturated conductivities (Ksat) are relatively small (relative to the draining-curve porosity). This is because the trapped air (volume) was removed from the porosity for the wetting curves. Also, the saturated conductivities (Ksat) are smaller for the wetting curves because the reduced water saturations (trapped air replacing water) effectively cause a smaller relative permeability which is lumped into the Ksat value for single-phase simulations. In multi-phase analysis, however, the trapped air should be left in the porosity, since the air mass is actually modeled in a multi-phase analysis. Hence, the draining curves were also used in the multi-phase analysis, but not in the single-phase analysis. In effect, the wetting curves with the smaller effective porosity would tend to increase the water and CCl$_4$ movement, but the smaller Ksat values (in the wetting curves) would tend to decrease the water and CCl$_4$ movement compared to movement expected from multi-phase-derived wetting curves (Lenhard 1992) or from the single-phase draining curves. Both the wetting and draining curves will need to be found from simultaneous curve fits in the future for multi-phase analysis.

The Stone's, van Genuchten/Mualem, and Brooks-Corey/Mualem relationships for three-phase relative permeabilities were given in Equations 5 to 8. The Brooks-Corey and van Genuchten parameters for each stratigraphic unit are given in Table 5 for both the imbibition (wetting) case and the draining (drying) case. Also listed in Table 5 are the base values of k*, the relative permeability of NAPL at irreducible water saturation, which are used in the Stone's methods. The base values for k* are the values originally assumed as appearing most reasonable. In the application of the Stone's methods, to be discussed in Section 2.3.4, it became necessary to evaluate the sensitivity of this parameter for the Hanford formation since this unit had the greatest effect on the mobilities of water and CCl$_4$.

One of the most important parameters in Stone's 2 method is k*, which is the relative permeability of the NAPL when the water saturation is equal to the residual (irreducible) water saturation. Several values of k* were used

in lieu of experimental data. Lower values of k^* make the NAPL more mobile than higher values.

In addition to the hydrologic properties that are required for modeling, Table 6 lists some other basic physical and chemical properties of CCl_4 that may be useful in this investigation.

Table 6. Useful Physical and Chemical Properties
of Carbon Tetrachloride.

Property	CCl_4	Water
Solubility in water	800 mg/L @ 20 °C	N/A
Vapor pressure	113.8 mm Hg @ 25 °C	24 mm Hg @ 25 °C
Saturated vapor concentration	754 mg/L	N/A
Henry's Law Constant, K_H (dimensionless)	9.4×10^{-1}	N/A
Liquid density	1.59 g/mL @ 20 °C	1.0 g/mL @ 25 °C
Vapor density	1.65	(air = 1.0)
Dielectric constant (dimensionless)	2.2	78.5
Surface tension	26.8 dynes/cm @ 20 °C	72.2 dynes/cm @ 20 °C
Interfacial tension (water-CCl_4)	45.0 dynes/cm	

Adapted from DOE-RL (1991).

2.3.2 Two-Dimensional and One-Dimensional Model - PORFLOW Code

Since the two-dimensional PORFLOW code had been used previously in the transmission oil problem (Piepho and Runchal 1991), it was considered feasible to forego the one-dimensional simulation.

When using PORFLOW, the van Genuchten relationships were used for both saturations and capillary pressures, and the Mualem extension by Parker was used for the three-phase permeabilities.

The first year of the two-dimensional simulation, which had low quantities for both water and CCl_4 sources, was performed without difficulty. Reasonable results were obtained for the first year. However, for the second year of simulation, the CCl_4 source term increased by almost a factor of 10. The run times on the Cray (a trademark of Cray Research Inc.) computer increased dramatically; 20 hours of Cray time would advance the simulation by about 0.3 of a year. Extrapolation of this information indicates that about 500 hours of Cray time would be required for the simulation of the 8 years of disposal to the crib. Considering that this simulation was only for one disposal facility and did not consider any redistribution of the water and CCl_4 within the vadose zone after cessation of disposal to the crib (an

additional 30 years would be required), it was deemed that the computer time required was too excessive.

Since the two-dimensional simulations were too computer intensive, effort was then switched to using PORFLOW in one-dimensional mode in the hope that some useful results could be obtained with more reasonable run times. However, the one-dimensional model would not run to completion; around the third year of simulation, time steps of one-millionth of a year would be required and in effect cause the simulation to hang up.

The main obstacle in completing the one-dimensional simulation was caused by the nonlinear relationship between the relative permeabilities for water and CCl_4 and their saturations, which caused the total sum of relative liquid permeabilities to be much less than one. In other words, when a saturation (either water or CCl_4) becomes slightly less than its maximum value of 1 (e.g., 0.9), then the effective hydraulic conductivity becomes much less than the saturated hydraulic conductivity (around 0.09 of the saturated hydraulic conductivity). Since the source terms for both water and CCl_4 were larger than their nonlinearly reduced effective hydraulic conductivities (Ksat times relative permeability) in the Palouse soil, both fluids would build up in the layer above the Palouse soil until there was no more room because a one-dimensional model does not permit lateral flow the way that a two-dimensional does. Once there was no more room in the top layer, the fluid pressures would increase dramatically, which caused extremely small time steps to be taken.

As noted above, the PORFLOW code was not able to simulate the two-phase flow of water and CCl_4 with a reasonable amount of computer time using the extended van Genuchten/Mualem theory by Parker for the multi-phase constitutive relationships. With this inability of PORFLOW to deal with these simulations, attention turned to the SAMFT2D code.

2.3.3 Two-Dimensional Model - SAMFT2D Code

The SAMFT2D code (Huyakorn et al. 1991) was developed under an initiative at Los Alamos National Laboratory (LANL) and funded by the U.S. Department of Energy (DOE) Office of Technology & Development. LANL has been identified as the lead site for the development of multi-phase vadose zone and ground-water codes. Westinghouse Hanford Company is applying SAMFT2D for LANL as part of the developmental (beta) testing of the model.

The primary advantages of the finite element SAMFT2D code are that (1) it makes use of the Newton-Raphson iteration scheme, which is much faster than the Picard and modified Picard schemes for multi-phase flow; (2) apparently a larger grid size (i.e., a smaller number of nodes) can be used for finite element multi-phase flow simulations than the grid size used by finite difference codes such as PORFLOW; and (3) the Stone's methods for the multi-phase relative permeability of NAPL is offered as an option as well as the van Genuchten/Mualem and Brooks-Corey extensions.

The first runs of SAMFT2D considered two-phase flow, that of water and NAPL. After difficulties were encountered in achieving reasonable results, the simulation was set up as a three-phase flow problem by adding the air

phase. Surprisingly, the three-phase simulation ran faster and with fewer problems of convergence than the two-phase simulation.

The grid used for numerical simulations with SAMFT2D contained 549 nodes, 61 in vertical direction and 9 in horizontal direction. The vertical discretization is shown in Table 7.

Table 7.   Vertical Discretization Data for Lithologic Units.

Layer	Depth (m)		Thickness (m)	No. of grid blocks	Material type
	Top	Bottom			
Hanford formation	0.0	31.40	31.41	30	1
Palouse Soils	31.40	34.08	2.68	3	2
Plio-Pleistocene	34.08	40.47	6.39	7	3
Middle Ringold	40.47	61.41	20.94	20	4

2.3.4 Multi-Phase Results

The primary accomplishments during FY 1992 were getting the SAMFT2D code running on the Cray computer and evaluating the constitutive relationships for the three-phase simulation of water, CCl_4, and air using the SAMFT2D code. This section discusses the results of this evaluation.

Ten anisotropic cases were simulated with the main purpose of quantifying and evaluating the four relative permeability relationships that are available in the SAMFT2D code. These constitutive relationships, which were modeled with both wetting and drying characteristic curves, are the Stone-1 and Stone-2 methods, the van Genuchten method with the Mualem extension, and the Brooks-Corey method with the Mualem extension. For the Stone-1 and Stone-2 methods it was also necessary to evaluate the sensitivity of the NAPL relative permeability parameter, k^*, which was defined in Section 2.3.1 (Table 5).

No isotropic cases were simulated for the multi-phase flow because the results for the single-phase simulations and field observations indicate that the Hanford soils are anisotropic. The simulations used horizontal saturated conductivities that were 10 times larger than the vertical conductivities that were presented in Table 5.

Discussion of the results of these methods follow along with the graphs generated in the simulations.

Stone-2 Method

Case 1 - Wetting Curve Results, Mobile CCl$_4$ (k* = .45 in Hanford formation)

Carbon tetrachloride saturations are shown in Figure 14 after 8 years of the entire source term using the wetting curves and k*,= 0.45.

Case 2 - Wetting Curve Results, Less Mobile CCl$_4$ (k* = .55 in Hanford formation)

The CCl$_4$ saturations shown in Figure 15 are for k* = 0.55. Inspection of Figures 19 and 20 reveals that CCl$_4$ is more mobile in case 1 than in case 2, illustrating the high sensitivity of the parameter k* in regard to the mobility of CCl$_4$. This high sensitivity to a single parameter is very undesirable, and essentially eliminates the Stone-2 model from consideration in future CCl$_4$ modeling at the Hanford Site.

Case 3 - Drying Curve Results, Mobile CCl$_4$ (k* = .45 in Hanford formation)

This case is the same as case 1 except that the drying (draining) characteristic curves were used instead of the wetting curves. The saturation results are shown in Figure 16 and should be contrasted with the case 4 results shown in Figure 17.

Case 4 - Drying Curve Results, Less Mobile CCl$_4$ (k* = .55 in Hanford formation)

The saturation results for case 4 are shown in Figure 17, and they should be contrasted with the case 3 results in Figure 21, which show more mobility. Again, the small difference in the k* value (0.55 for case 4 versus 0.45 for case 3) causes a big difference in the CCl$_4$ mobility, a further illustration of the undesirability of the Stone-2 method.

Stone-1 Method

Case 5 - Wetting Curve Results

The CCl$_4$ saturations are shown after 8 years of sources in Figure 18 assuming the wetting characteristic curves. Using k* = 0.45, the mobility of CCl$_4$ with the Stone-1 method is less than that with the Stone-2 method (case 1).

Case 6 - Drying Curve Results

The CCl$_4$ saturations using the drying characteristic curves and k* = 0.45 are shown in Figure 19. As expected, the plumes do not move as much with the drying curves and their higher porosities as with the wetting curves and their corresponding smaller porosities even though the Ksat values are larger for the drying curves.

Figure 14. Carbon Tetrachloride Saturation at 8 Years,
Wetting Curves, Stone-2, $k^* = 0.45$.

Wet. Curves
Anisotropic
Stone's 2
Kstar = 0.45

Figure 15. Carbon Tetrachloride Saturation at 7.5 Years,
Wetting Curves, Stone-2, $k^* = 0.55$.

Wet. Curves
Anisotropic
Stone's 2
Kstar = 0.55

Figure 16. Carbon Tetrachloride Saturation at 8 Years,
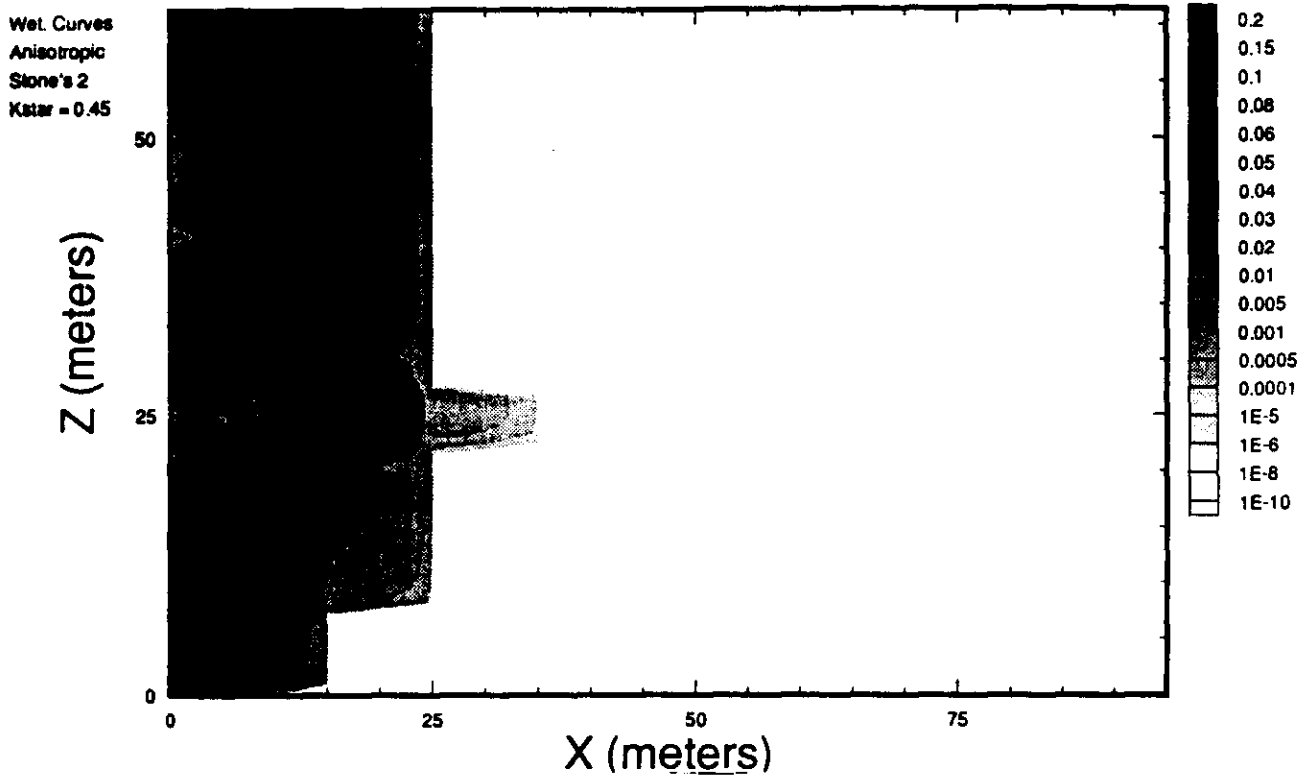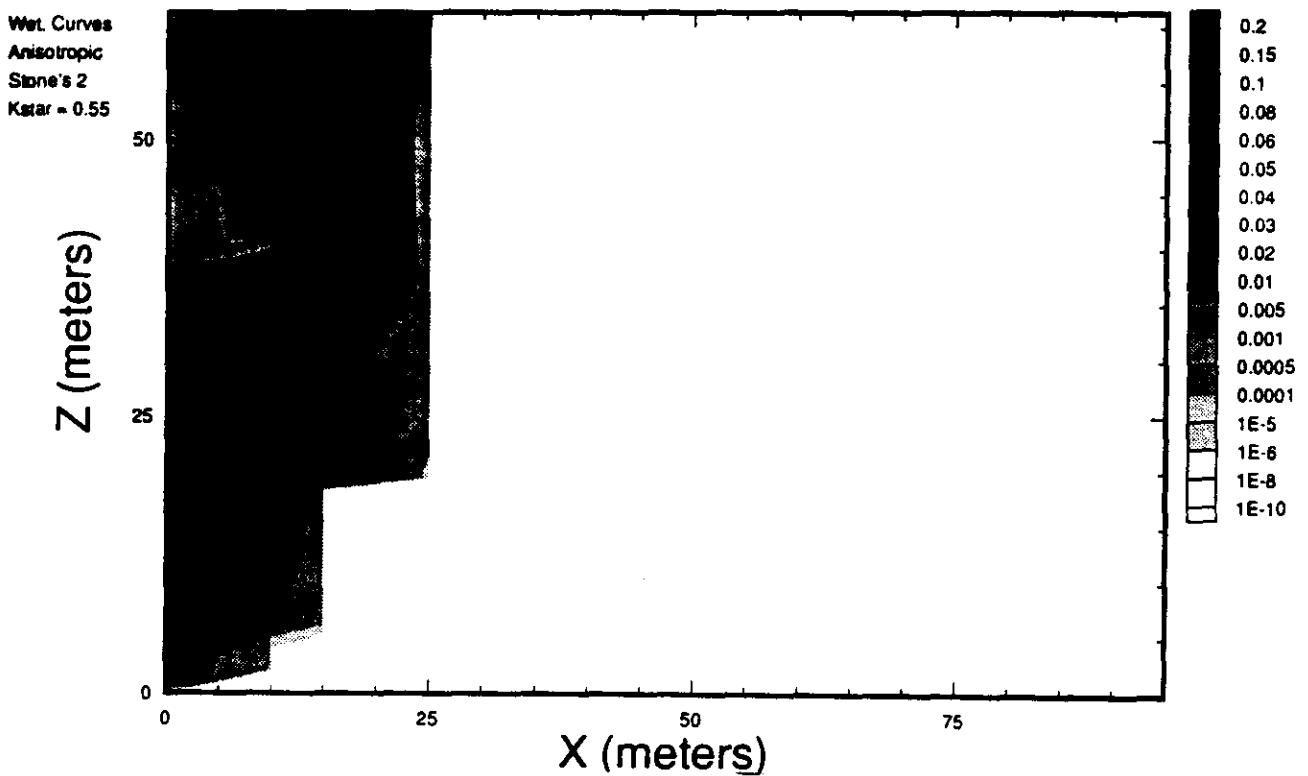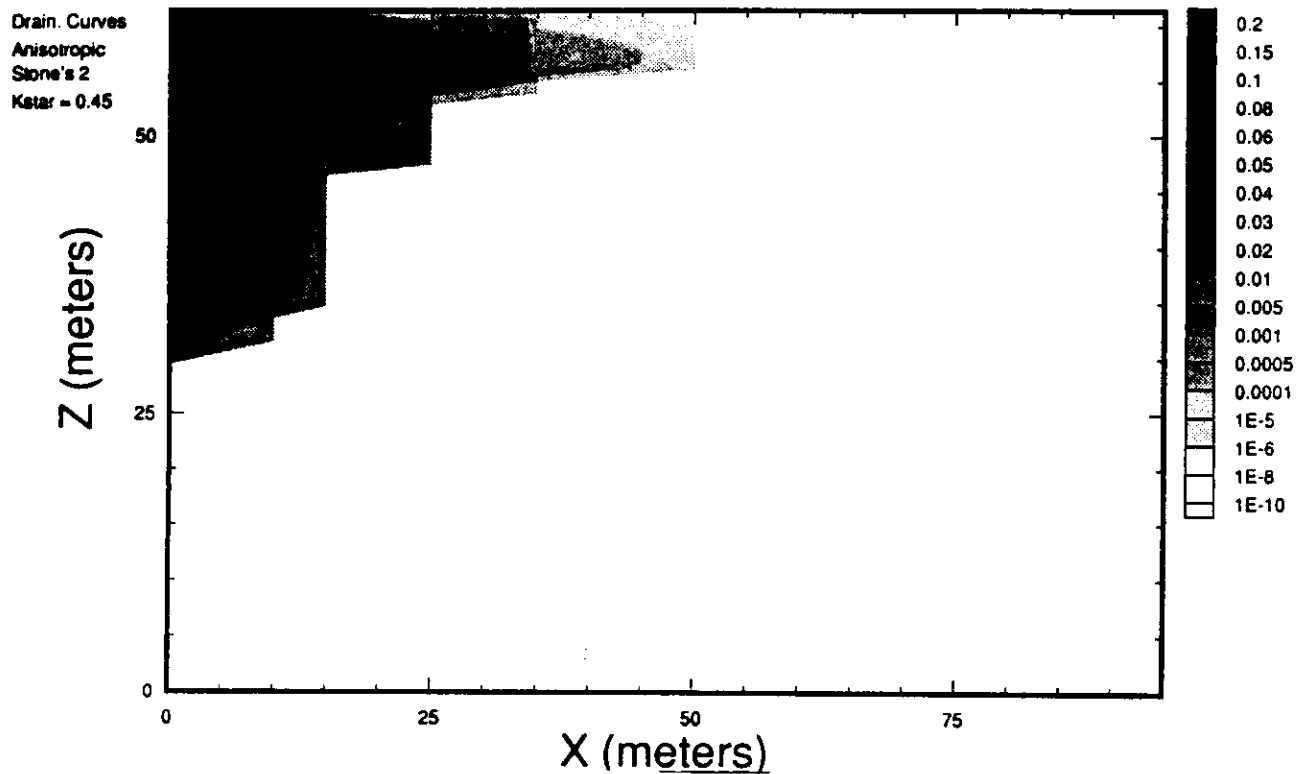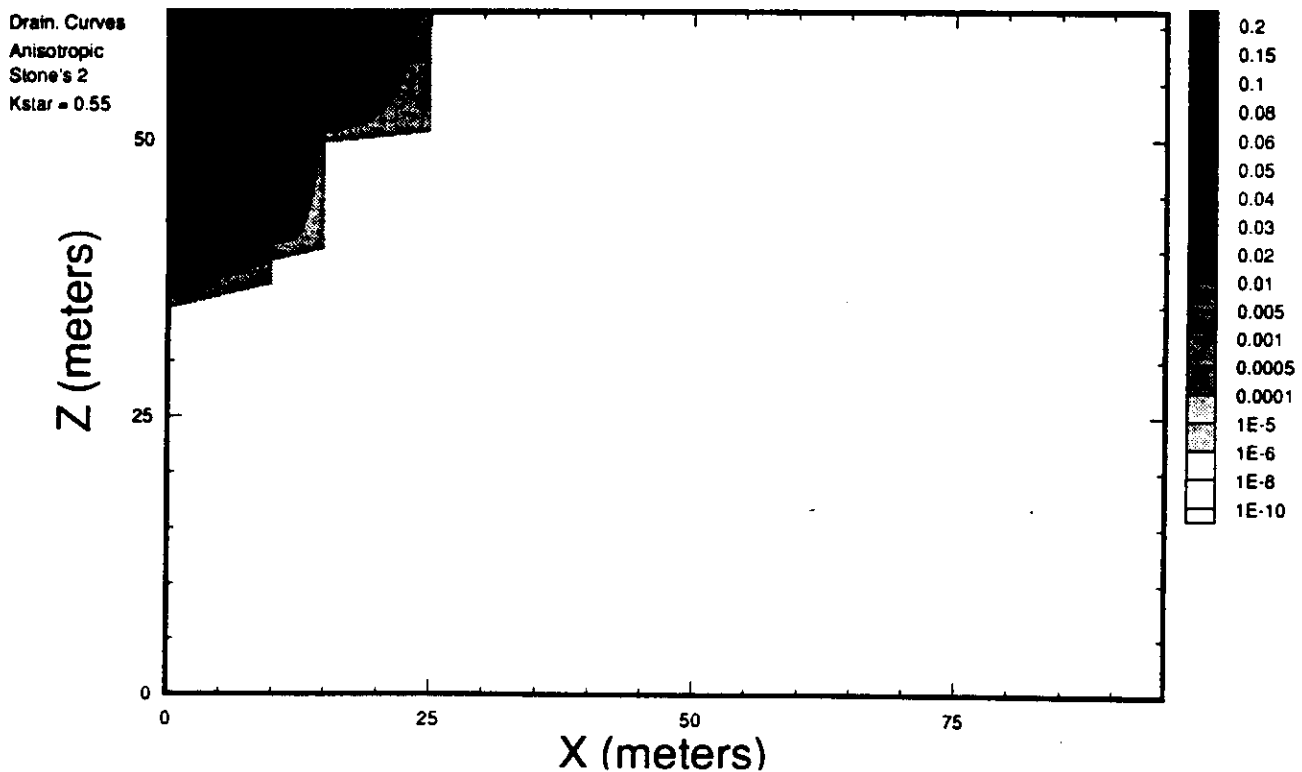Drying Curves, Stone-2, $k^* = 0.45$.

Figure 17. Carbon Tetrachloride Saturation at 8 Years,
Drying Curves, Stone-2, $k^* = 0.55$.

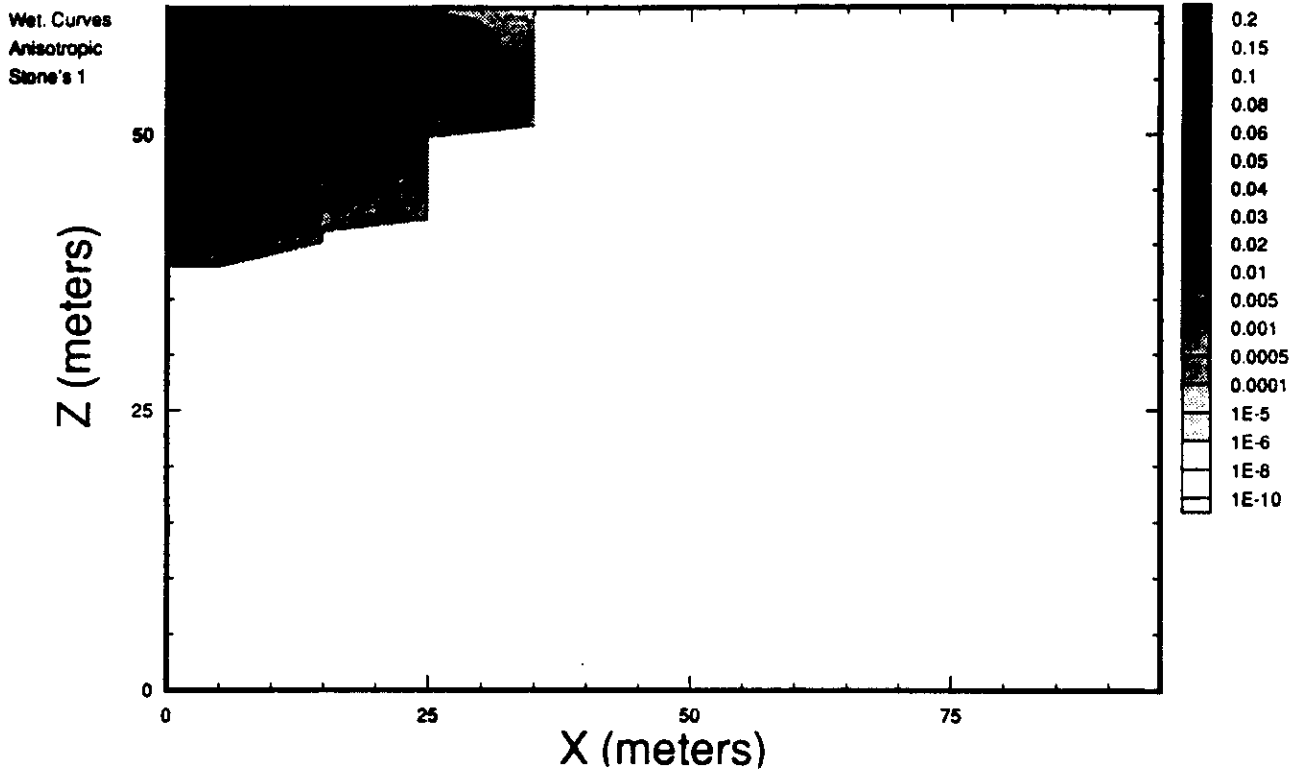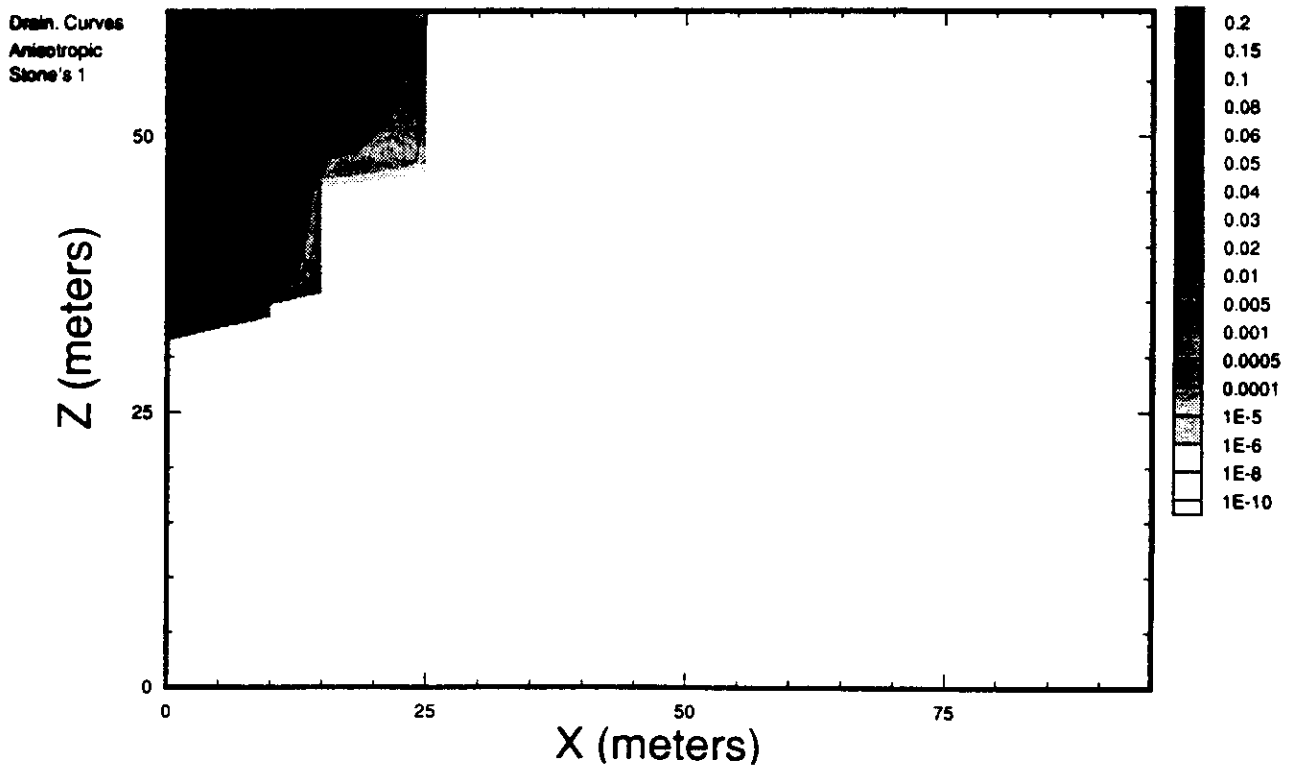Figure 18. Carbon Tetrachloride Saturation at 8 Years, Wetting Curves, Stone-1, k* = 0.45.

Wet. Curves
Anisotropic
Stone's 1

Figure 19. Carbon Tetrachloride Saturation at 8 Years, Drying Curves, Stone-1, k* = 0.45.

Drain. Curves
Anisotropic
Stone's 1

van Genuchten/Mualem Extension

Case 7 - Wetting Curve Results

The CCl_4 saturations are shown at the of 4 years, 6 years, 8 years, and 10 years in Figures 20a to 20d. This plume is the fastest moving plume in all of the simulations. The corresponding water saturations are shown in Figures 21a and 21b for the end of 4 years and 8 years. The high water saturations cause the CCl_4 to move more horizontally.

Case 8 - Drying Curve Results

The CCl_4 saturations, assuming the drying curves, at the end of 4, 6, 8, and 10 years are shown in Figures 22a to 22d. The water saturations at the end of 4 and 8 years are shown in Figures 23a and 23b. As expected the plumes did not move as much as when wetting curves are assumed.

Brooks-Corey/Mualem Extension

Case 9 - Wetting Curve Results

The CCl_4 and water saturations, using the wetting curves, at the end of 8 years are shown in Figures 24 and 25, respectively. Apparently, the Brook-Corey model does not permit the NAPL relative permeabilities to become as large as in the van Genuchten model.

Case 10 - Drying Curve Results

The CCl_4 and water saturations, using the drying curves, at the end of 8 years are shown in Figures 26 and 27, respectively. Apparently, the CCl_4 is more mobile when drying curves are used rather than when wetting curves are used. This aspect of the Brooks-Corey model, when combined with the extended Mualem theory, needs to be investigated more. In the other models, the wetting curves will promote more NAPL mobility than the drying curves.

Longer Term Simulation, van Genuchten/Mualem Extension

Case 11 - Drying Curve Results

Although somewhat premature due to the need for further investigation of several parameters, a 28-year simulation was performed in a simple approach as to what may be expected during 20 years of redistribution of CCl_4 following 8 years of effluent disposal. Figure 28 illustrates the results of this simulation, and this figure should be compared with Figures 22a through 22d, especially Figure 22d. Figure 28 is seen to have the same general shape as Figure 22d, but with a slightly lower concentration of CCl_4 saturation indicating only a slight change in 20 years of distribution. However, this simulation is weak in that no vapor phase was incorporated for the CCl_4, so evaporation of the residual CCl_4 is not considered. As discussed in Chapter 4.0, the vapor phase is planned for incorporation next year.

Figure 20a. Carbon Tetrachloride Saturation at 4 Years,
Wetting Curves, van Genuchten/Mualem Extension.

Figure 20b. Carbon Tetrachloride Saturation at 6 Years,
Wetting Curves, van Genuchten/Mualem Extension.

**Figure 20c. Carbon Tetrachloride Saturation at 8 Years,
Wetting Curves, van Genuchten/Mualem Extension.**

**Figure 20d. Carbon Tetrachloride Saturation at 10 Years,
Wetting Curves, van Genuchten/Mualem Extension.**

Figure 21a.   Water Saturation at 4 Years, Wetting Curves,
van Genuchten/Mualem Extension.

Figure 21b.   Water Saturation at 8 Years, Wetting Curves,
van Genuchten/Mualem Extension.
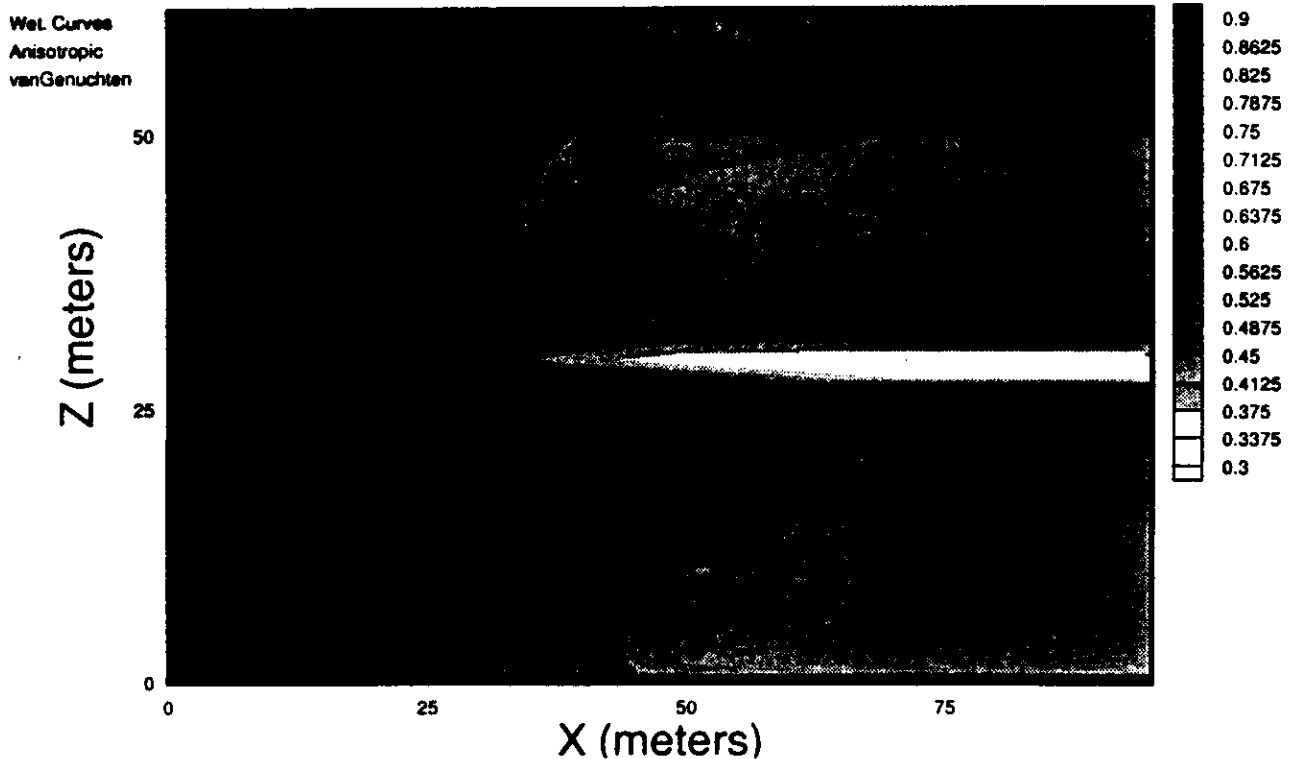
Figure 22a. Carbon Tetrachloride Saturation at 4 Years,
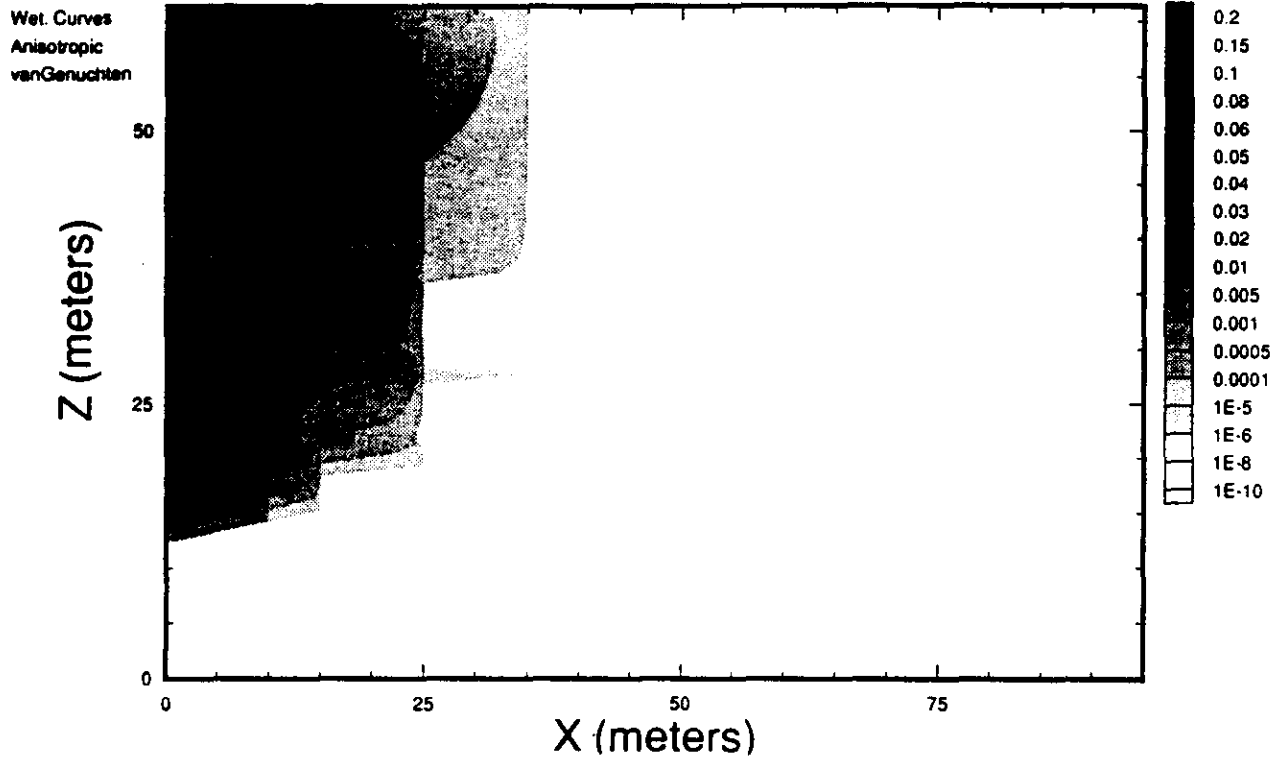Drying Curves, van Genuchten/Mualem Extension.

Figure 22b. Carbon Tetrachloride Saturation at 5.7 Years,
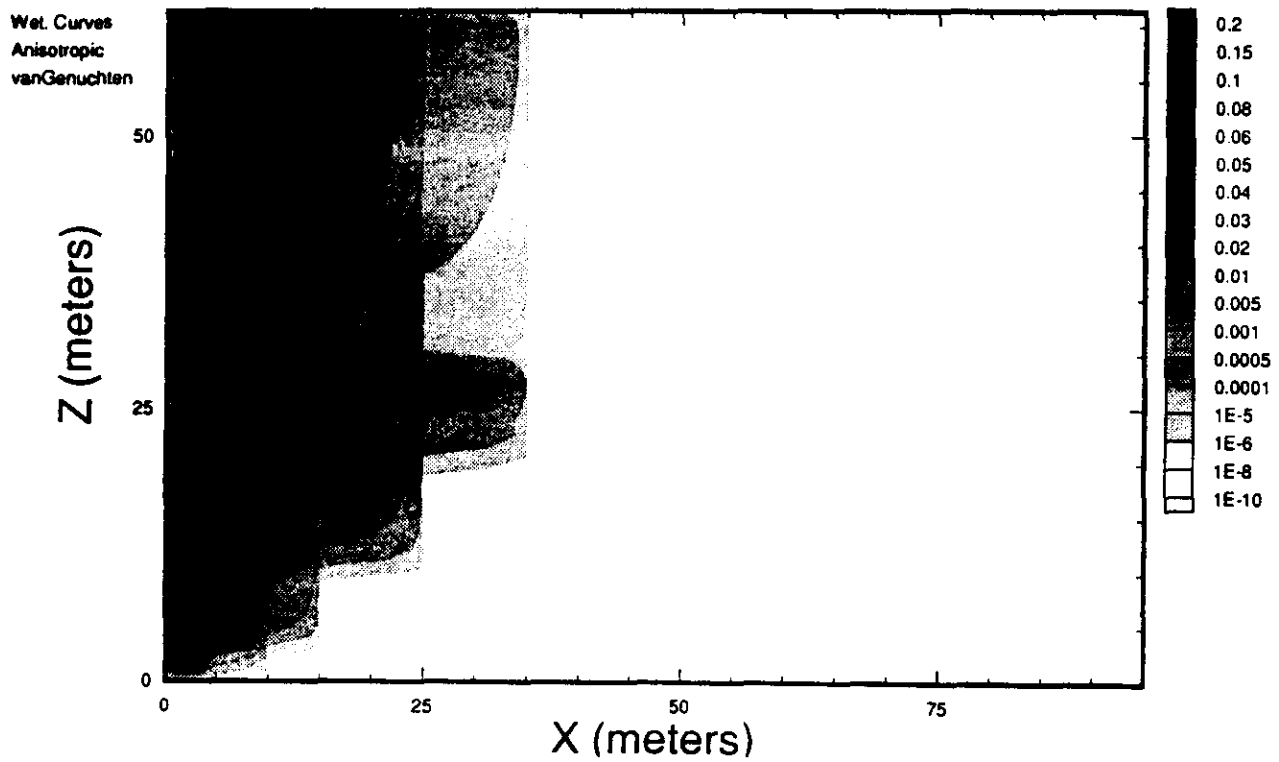Drying Curves, van Genuchten/Mualem Extension.

Figure 22c. Carbon Tetrachloride Saturation at 7.6 Years,
Drying Curves, van Genuchten/Mualem Extension.

Figure 22d. Carbon Tetrachloride Saturation at 10 Years,
Drying Curves, van Genuchten/Mualem Extension.

Figure 23a. Water Saturation at 4 Years, Drying Curves,
van Genuchten/Mualem Extension.

Drain. Curves
Anisotropic
vanGenuchten

0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
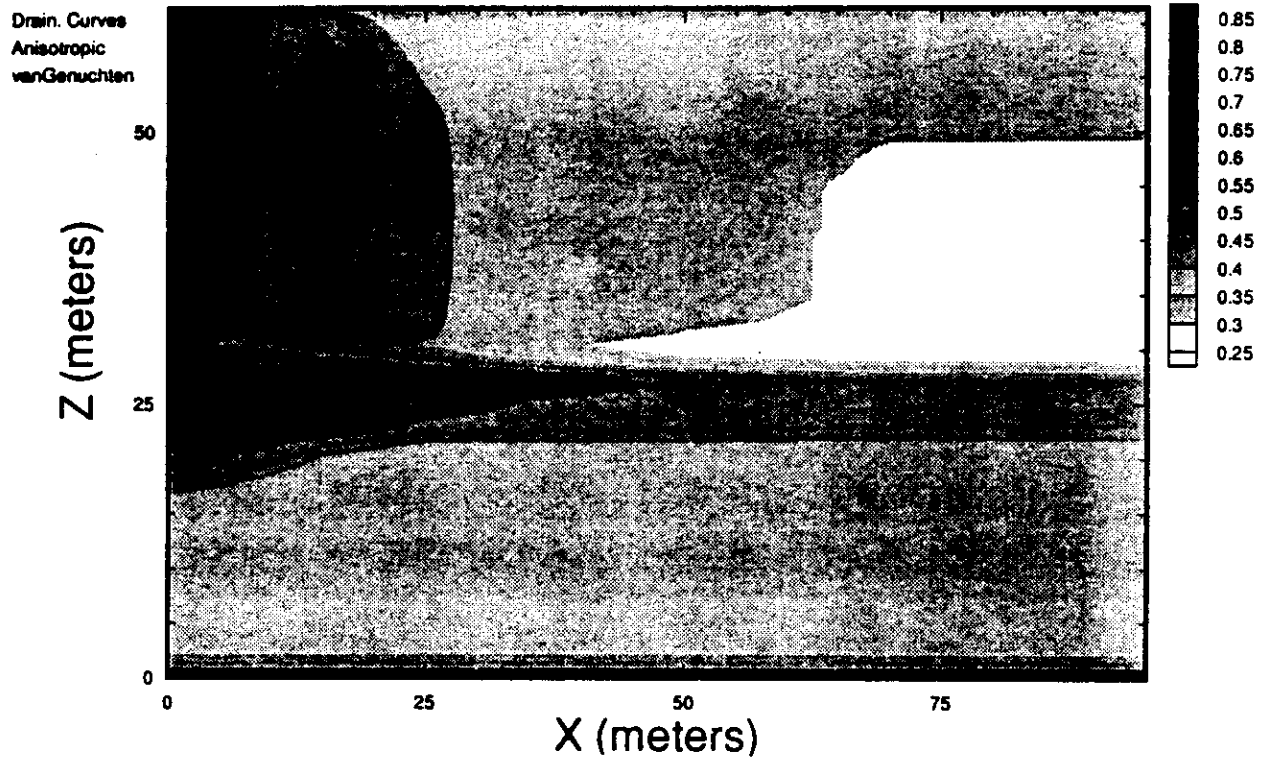
Figure 23b. Water Saturation at 7.6 Years, Drying Curves,
van Genuchten/Mualem Extension.

Drain. Curves
Anisotropic
vanGenuchten

0.85
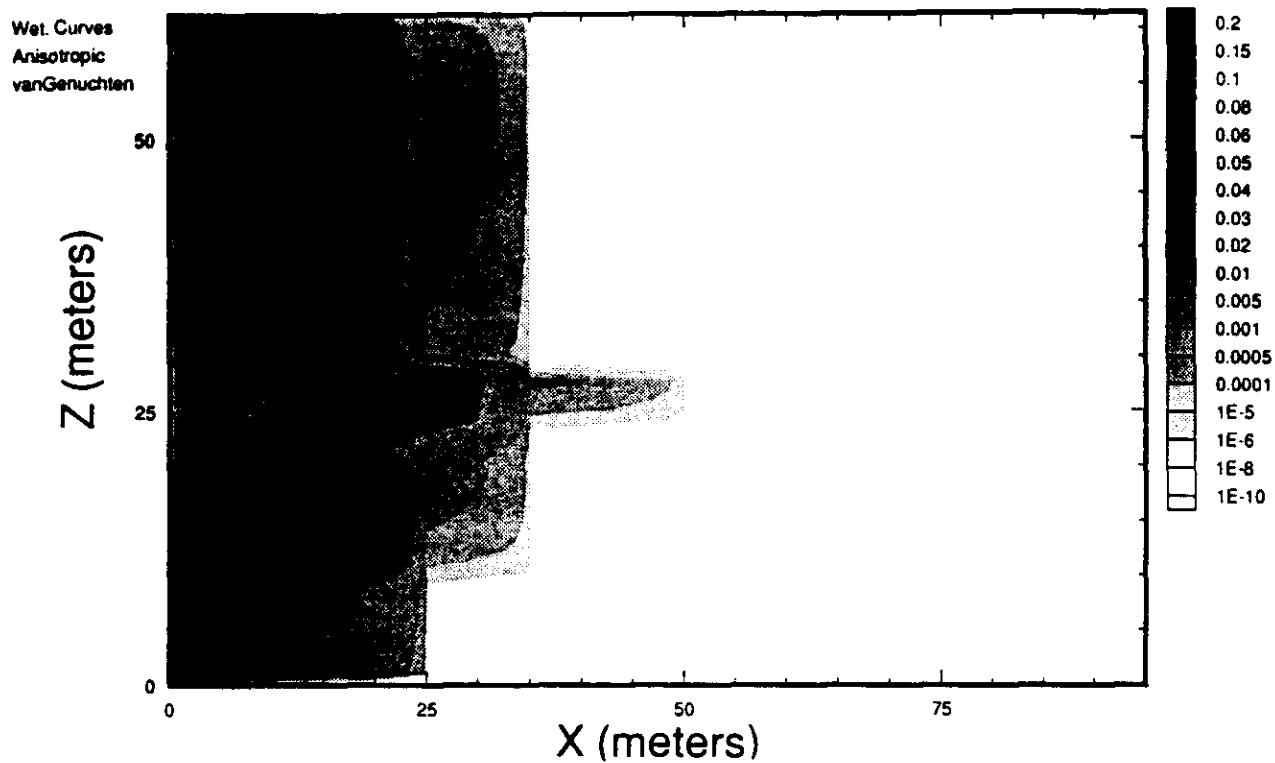0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
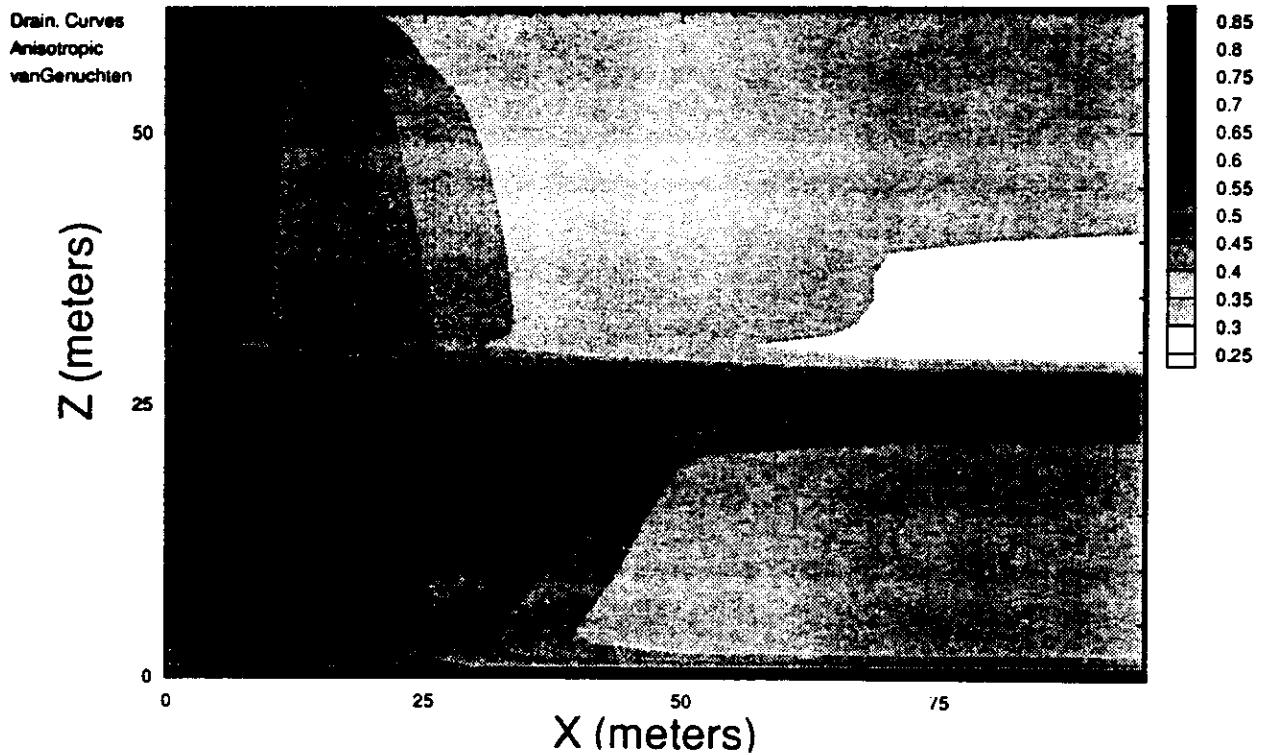
Figure 24.   Carbon Tetrachloride Saturation at 8 Years,
Wetting Curves, Brooks-Corey/Mualem Extension.
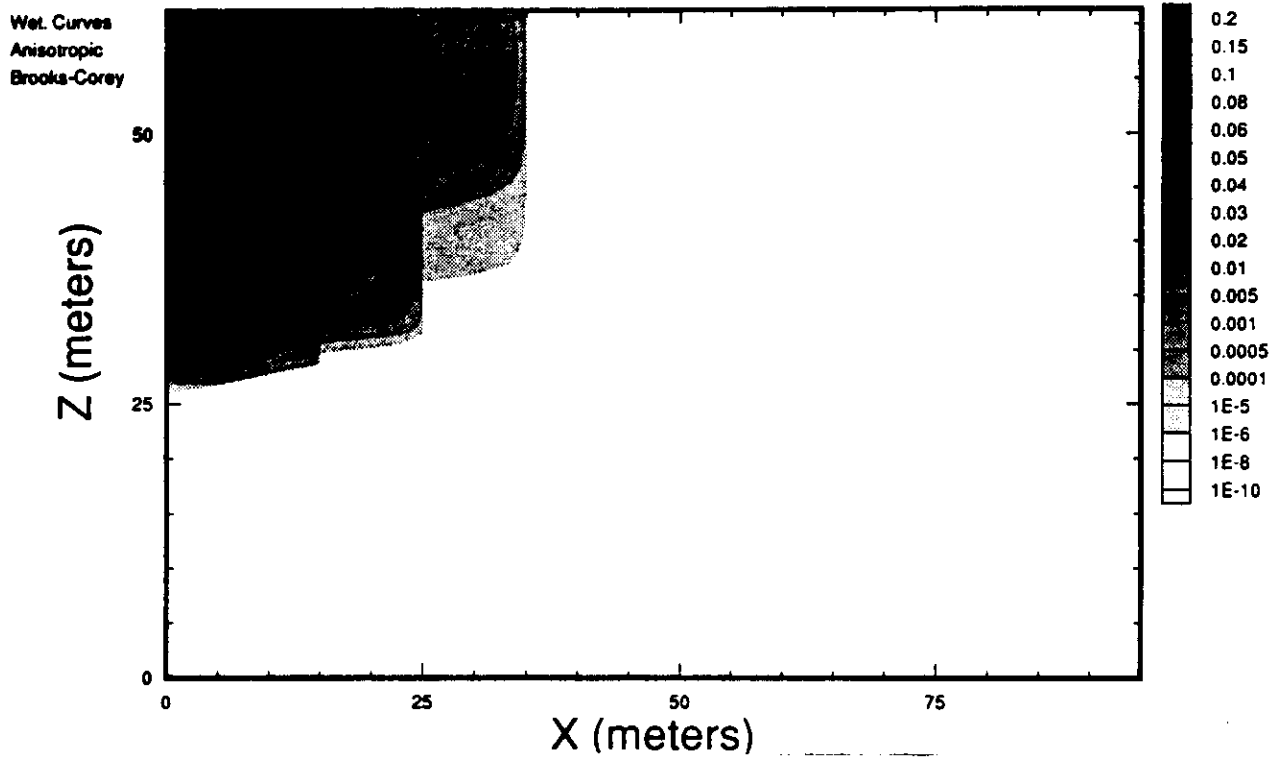
Figure 25.   Water Saturation at 8 Years, Wetting Curves,
Brooks-Corey/Mualem Extension.
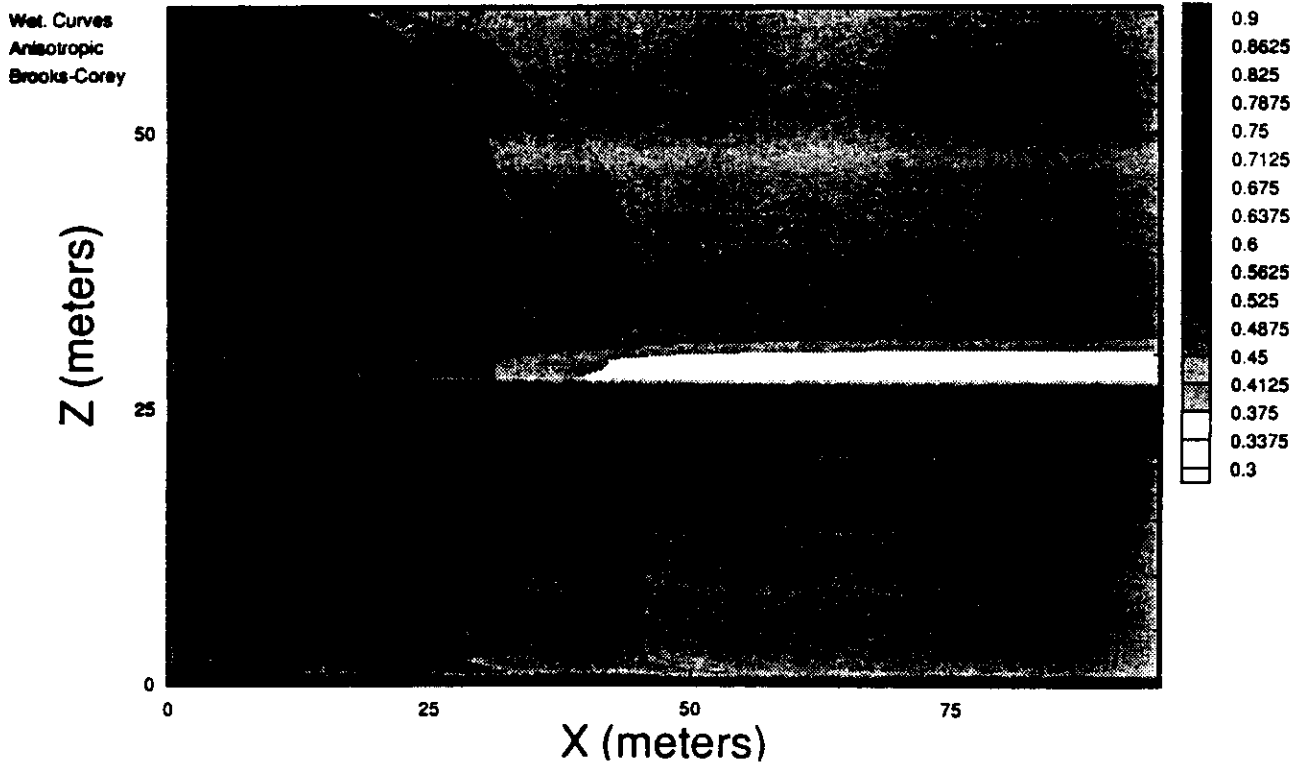
Figure 26. Carbon Tetrachloride Saturation at 8 Years, Drying Curves, Brooks-Corey/Mualem Extension.
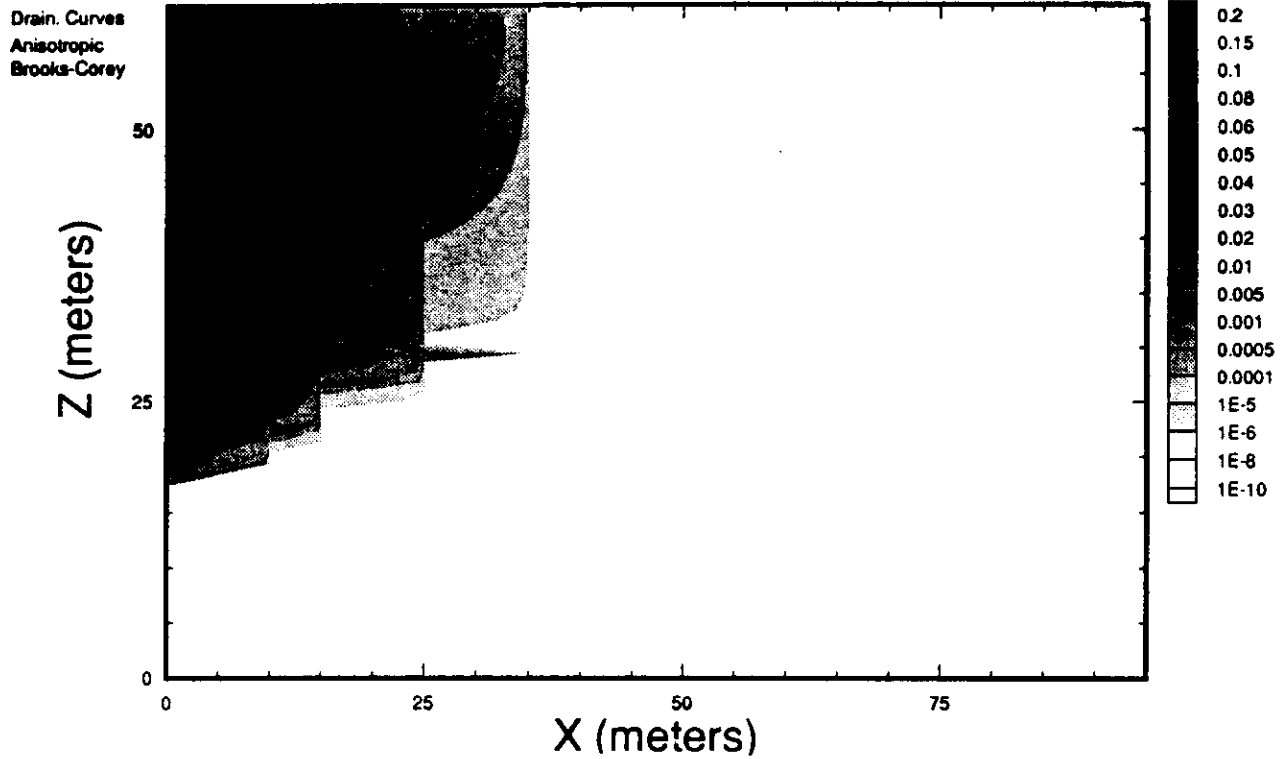
Figure 27. Water Saturation at 8 Years, Drying Curves, Brooks-Corey/Mualem Extension.

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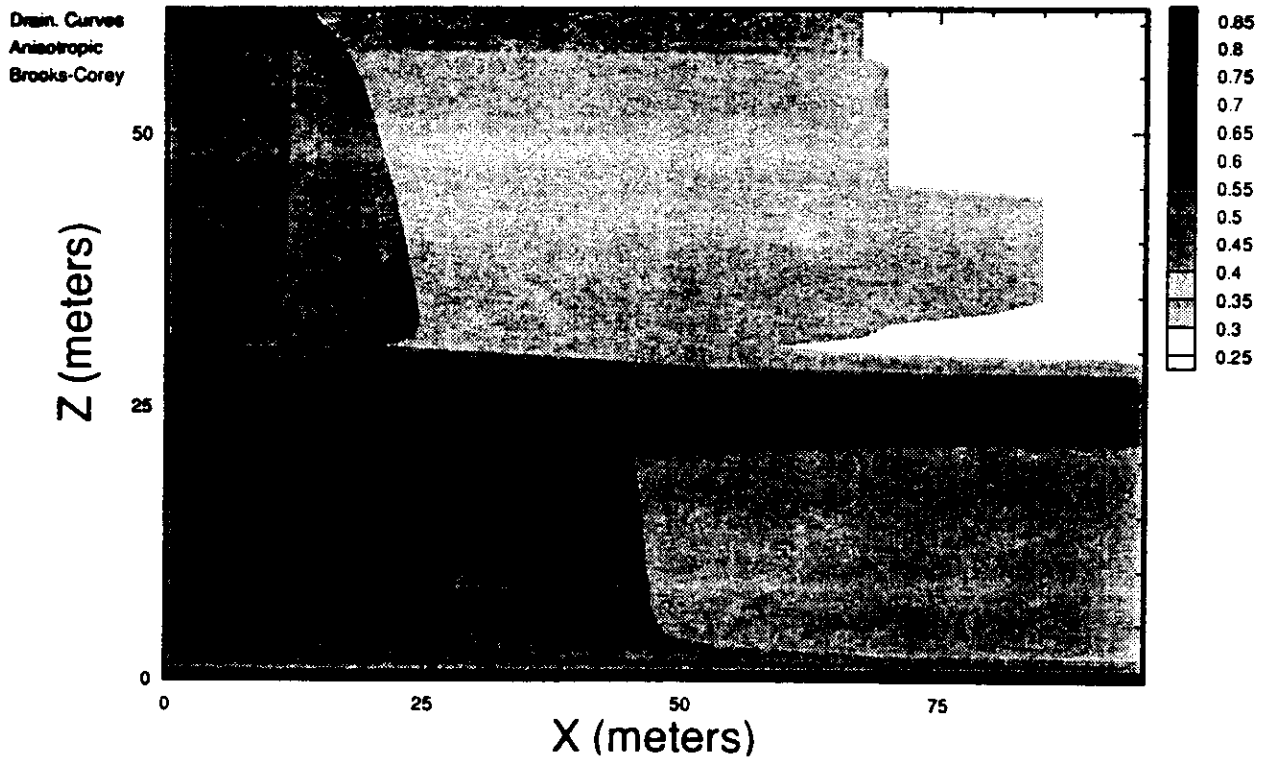
Figure 28. Carbon Tetrachloride Saturation at 28 Years,
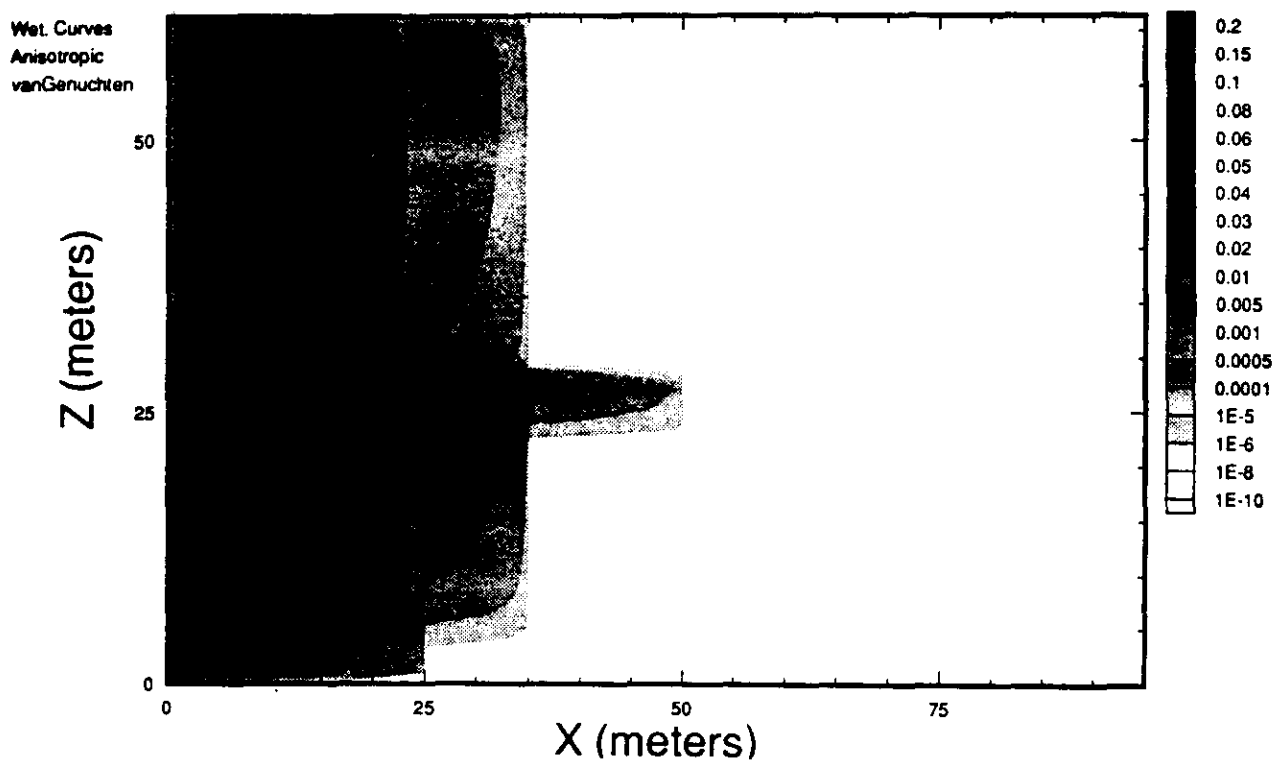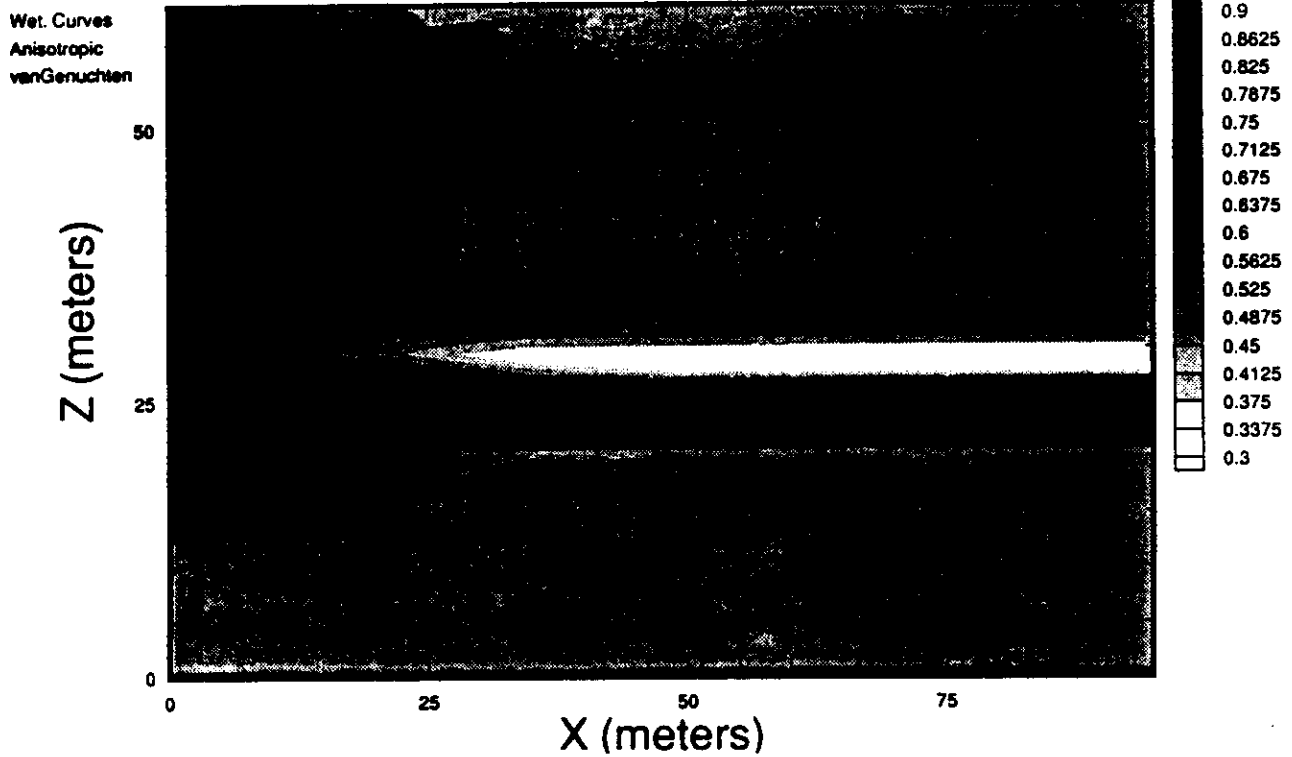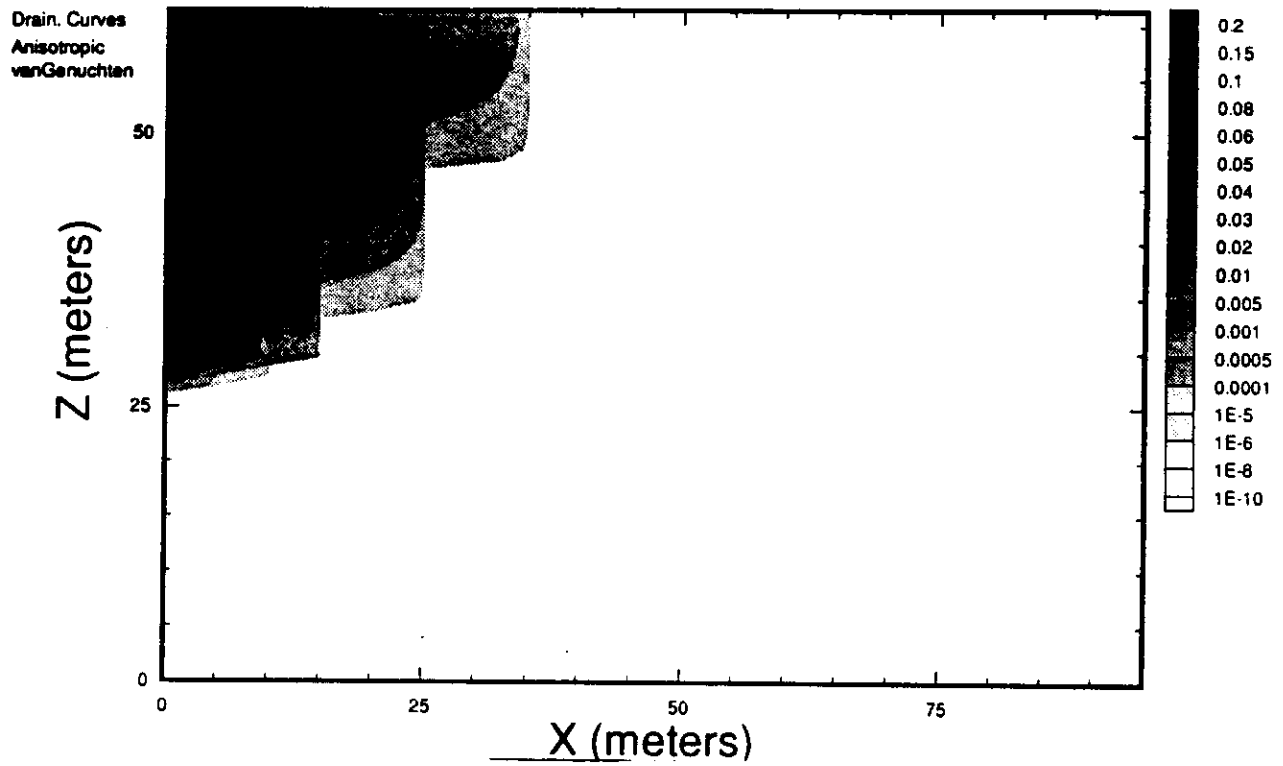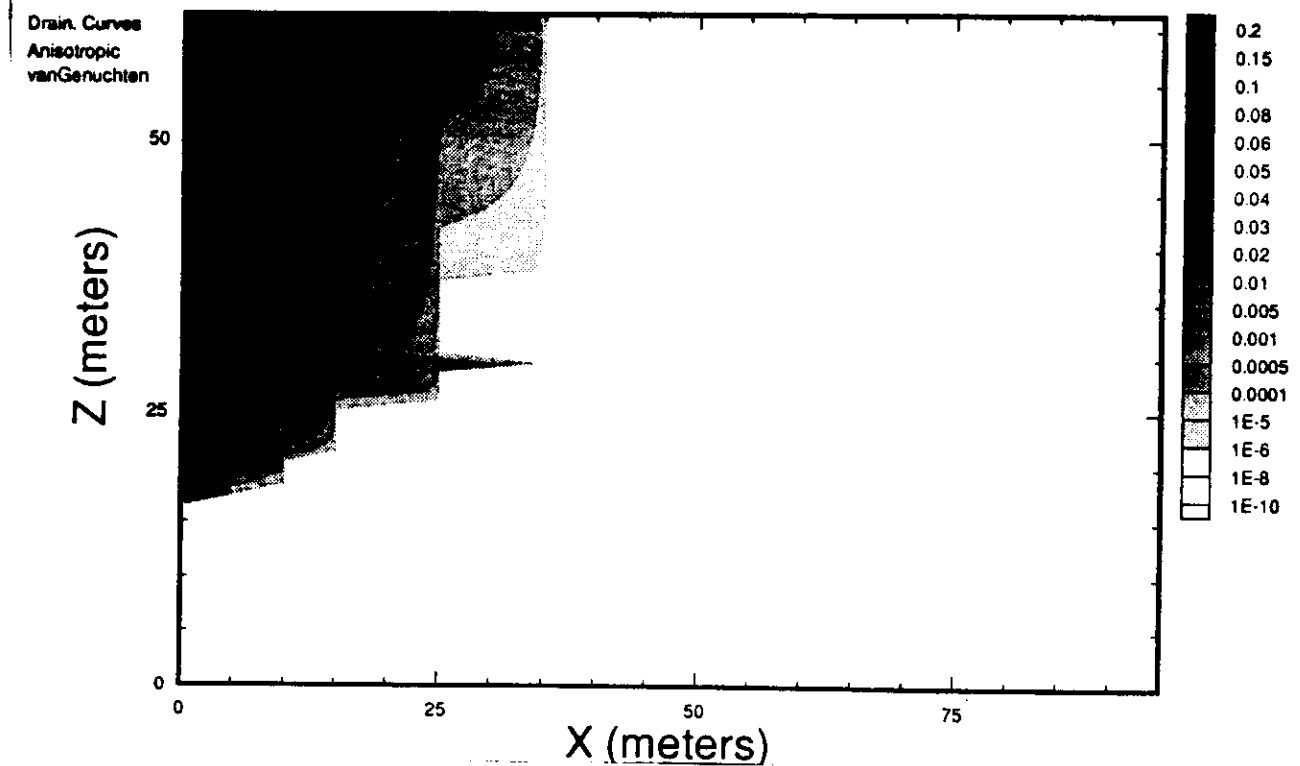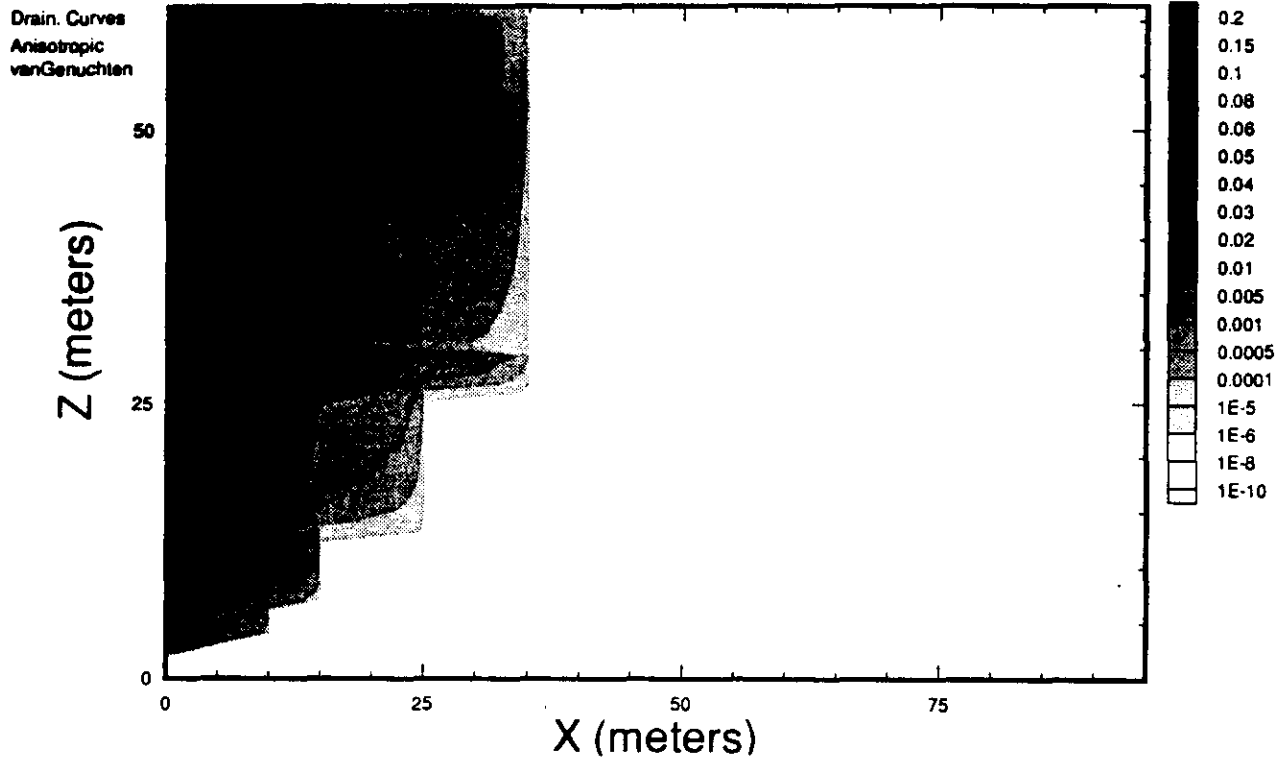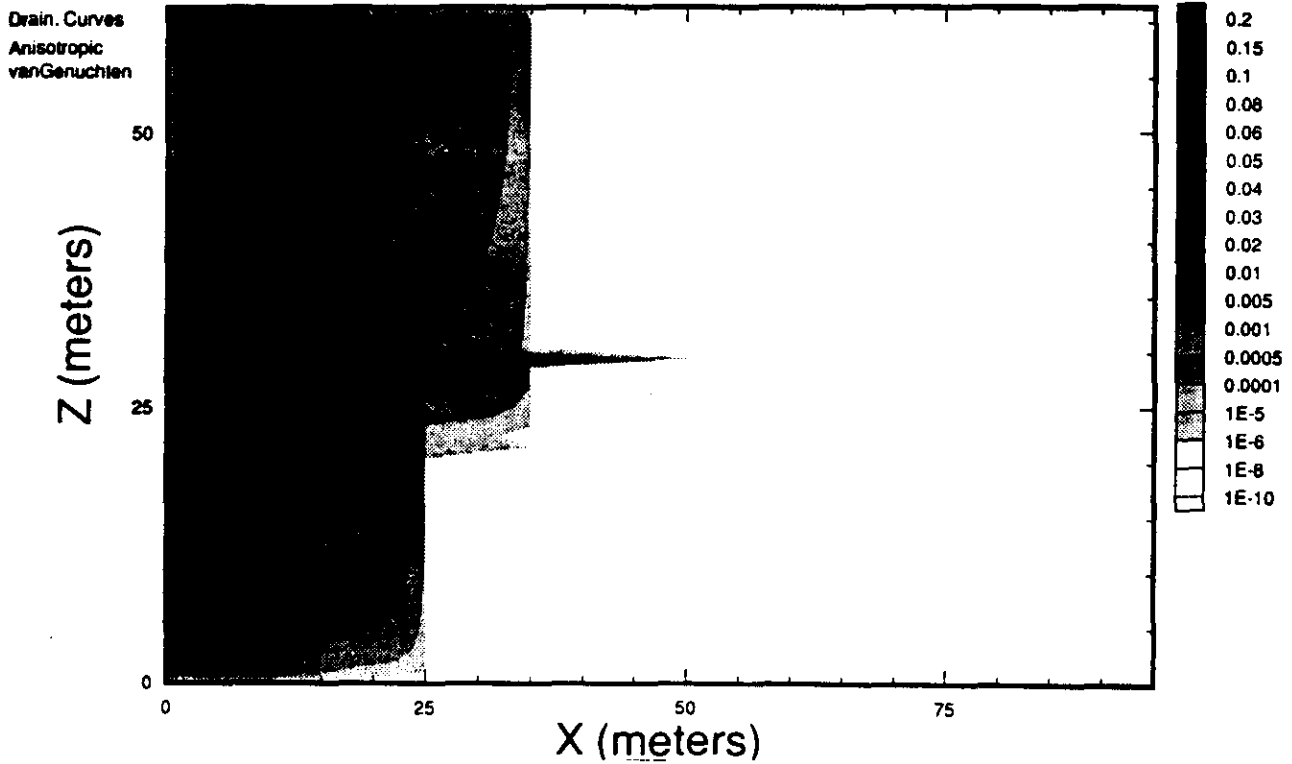Drying Curves, van Genuchten/Mualem Extension.
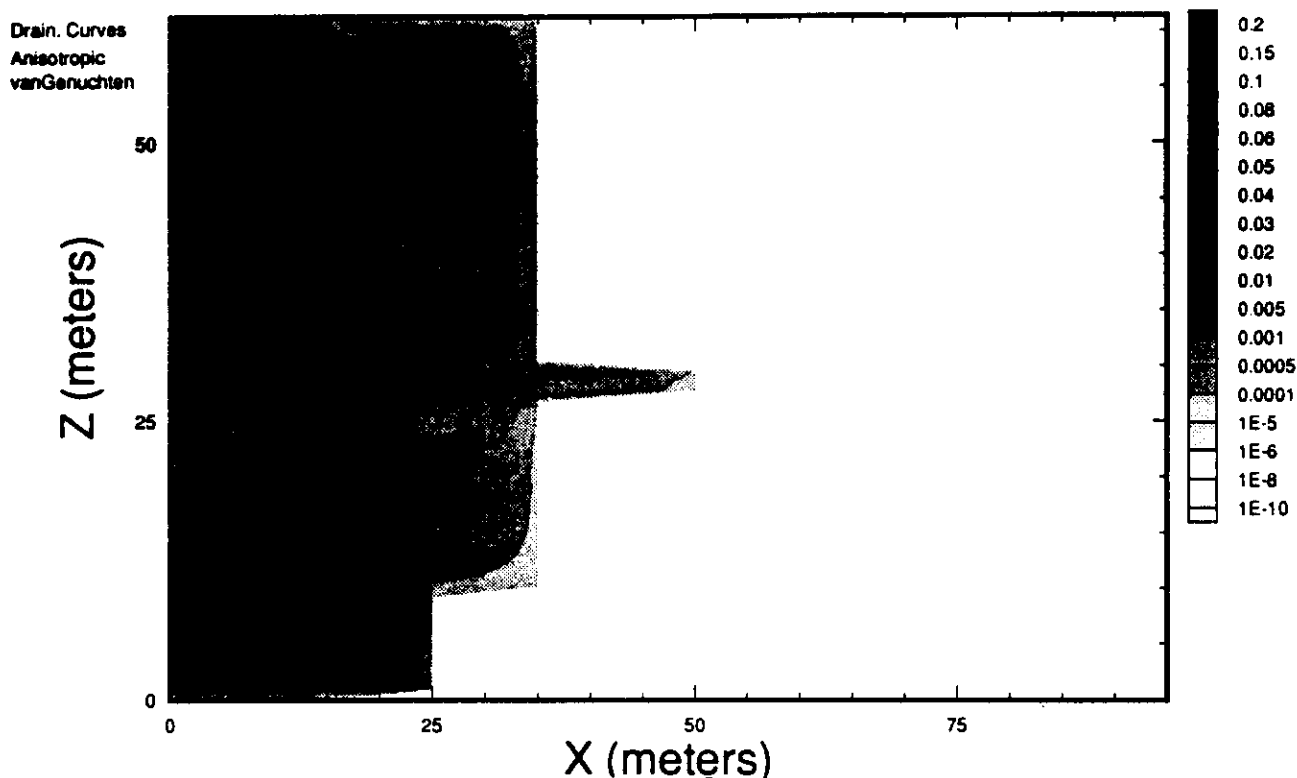
In summary, the work performed in FY 1992 suggests that the
van Genuchten/Mualem method of treating the relative permeabilities for multi-
phase flow is most appropriate. Also, the use of drainage curves, as opposed
to wetting curves, is believed to permit a more realistic simulation since the
wetting curves contain an allowance for porosity as discussed in
Section 2.3.1.

3.0 CONCLUSIONS

The three-phase flow modeling suggests that it is possible that the CCl_4
could have migrated from the 216-Z-9 Trench through the vadose zone to the
ground water, irrespective of the issue of whether any CCl_4 moved down the
outside of a well casing or through any fractures. However, several
uncertainties are associated with this simulation that should be investigated
further. It is also necessary to collect field data on the occurrence of NAPL
at residual saturation in the sediments beneath the disposal facility.
Without this information for calibration, no model application can provide
definitive information.

The single-phase simulations performed indicated that the Early Palouse
soil with a lower conductivity layer functions as an impediment to the
downward migration of moisture and suggest that about 6 years would be
required for water to reach that layer. The hydraulic parameters used in the

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single-phase simulation yielded reasonable results indicating that they are "ball park" values for multi-phase simulation.

The three-phase flow simulations suggest that most of the free liquid CCl_4 that has not evaporated should now be located in the Plio-Pleistocene (caliche) and Early Palouse layers or in the ground water. Horizontal spread in the vadose zone appears to be minimal even though anisotropy was assumed. Two uncertainties that could affect these results are the dip (inclination) of the Early Palouse and Plio-Pleistocene layers (these layers were treated as horizontal in this study) and the assumed initial moisture content within the geohydrologic units of the unsaturated zone.

The Stone's methods of dealing with three-phase relative permeabilities appear to be inadequate for modeling CCl_4 movement because of the high sensitivity of CCl_4 movement to the k^* permeability parameter. The extended Mualem model, with either the Brooks-Corey or van-Genuchten relationships, for the three-phase NAPL permeabilities appears to be better than either of the Stone's methods for modeling CCl_4 in Hanford Site soils.

Concerning numerical aspects, algorithms within computer codes were identified that are needed to perform successful simulations. The Newton-Raphson iteration scheme is more advantageous than the Picard or modified Picard methods in solving the numerical equations. However, the main numerical feature is to be able to solve the coupled pressure heads simultaneously for each cell and not in segregated fashion where the pressure head of one phase is solved for all the cells before the pressure head of a second phase is solved. PORFLOW, a segregated code, gives very accurate mass balances, but the computer run times are very long. SAMFT2D uses the Newton-Raphson linearization method and solves the pressure heads simultaneously for all the phases, which makes it faster than PORFLOW for multi-phase problems.

Summary of model accomplishments: After resolving difficulties with the SAMFT2D code, it is now operational on the Cray. After investigating the effects of four relative permeability relations, the two Stones' methods have been discarded in favor of the van Genuchten and Brooks-Corey relations combined with the extended Mualem theory. Since van Genuchten parameters are more readily available for Hanford Site sediments, the van Genuchten relationships will be used in future modeling endeavors.

4.0 RECOMMENDATIONS

The first recommendation is to examine the sensitivity of the initial conditions of moisture content. This study assumed a 5-cm/year recharge, which caused a high initial moisture content. The 5-cm/year value was a widely assumed value at the time this work was initiated. However, it appears that a recharge rate of 0.1 cm/year or less is more likely, which would cause a lower moisture content. With less initial moisture, there is more space for NAPL storage as residual saturation and the water and CCl_4 plumes are expected to be less mobile and not travel as far in the vadose zone.

The second recommendation is to investigate what effect the dip of the Early Palouse and Plio-Pleistocene (caliche) layers will have on the CCl_4 distribution. For the present study, all soil layers were assumed to be horizontal, which does not promote horizontal migration like an inclined layer would. The CCl_4 would move down dip on an inclined layer with less penetration, and it is of interest to evaluate to what extent this would reduce or eliminate the migration of CCl_4 to ground water.

After knowing more about the distribution of the liquid CCl_4, as expressed in the above recommendations, the next step would be to model the vapor phase of CCL_4. Modeling the gaseous CCl_4 movement can be done most accurately if the phases of water, liquid CCl_4, and air are modeled in a transport simulation in such a manner that gaseous CCl_4 is treated as a component of the air phase. One reason for the improved accuracy is that liquid CCl_4 starts evaporating as soon as it hits the trench, and the liquid CCl_4 plume continues to move for many years, evaporating as it moves. This approach would provide a more realistic simulation of the redistribution of CCl_4, especially the gaseous phase, after the cessation of its disposal. This would address the weakness in the work accomplished to date, the lack of consideration of the vapor phase, as noted in Section 2.3.4. One main drawback in modeling all three phases simultaneously is the large computational effort that usually is required. Because of the demanding computational requirements, very few codes are available that can solve all three phases. However, the SAMFT2D code apparently is one of the few codes that has the capability to model the vapor phase (i.e., water, air, liquid CCl_4, and gaseous CCl_4 can be modeled in one run).

The work in FY 1993 will be directed toward the 216-Z-1A Tile Field and the 216-Z-18 Crib in addition to the 216-Z-9 Trench, which has been emphasized in FY 1992.

The determination and measurement of NAPL in a subsurface environment is not an easy task. However, it is most important to have this information for a successful simulation since it provides an opportunity to calibrate the model, i.e., select appropriate reasonable parameters that permit the simulated conditions to match those observed in the field environment.

In discussing the determination and measurement of NAPLs with several leaders of the field, three papers have been identified that suggest methods of making these determinations and measurements. It is recommended, apart from this modeling investigation, that the work of Cary et al. (1991), Cohen et al. (1992), and Feenstra et al. (1991) be investigated and incorporated into the ERA field work at the earliest opportunity if any of these methods appear promising for this activity. On a cursory basis, the work of Cary et al. (1991) appears that it might be appropriate.

Accomplishment of these recommendations in FY 1993 should permit a reasonable estimation of where the CCl_4 is located in the subsurface environment, including predictions of the phases and concentrations.

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